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CHARACTERISTIC LINES OF A HYPERSURFACE V_n IMBEDDED IN A RIEMANNIAN V_{n+1}

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1. Introduction

Upon a surface of positive curvature there is a unique conjugate system for which the angle between the directions at any point is the minimum angle between conjugate directions at that point. This system of lines is called *characteristic lines* or *mean-conjugate net* (Eisenhart, 1909, 1947). The object of the present paper is to obtain the equation of characteristic lines of a hypersurface in a Riemannian V_{n+1} and to discuss some properties of these curves.

2. Hypersurface in V_{n+1}

Consider a hypersurface V_n of co-ordinates x^i, $i = 1, 2, \ldots . n$ and metric

$$ds^2 = g_{ij}dx^i dx^j, \tag{2.1}$$

imbedded in a V_{n+1} of co-ordinates y^α, $\alpha = 1, 2, \ldots . n+1$, and metric

$$ds^2 = a_{\alpha\beta}dy^\alpha dy^\beta. \tag{2.2}$$

We then have the relation

$$g_{ij} = a_{\alpha\beta}\, y^\alpha{}_{,i}\, y^\beta{}_{,j} \tag{2.3}$$

where (,) followed by an index indicates covariant derivative with respect to the x with that index. If N^α, $\alpha = 1, 2, \ldots . n+1$, be the contravariant components of the unit normal to V_n,

$$a_{\alpha\beta}\, N^\alpha N^\beta = 1, \tag{2.4}$$

$$y^\alpha{}_{;ij} = \Omega_{ij}N^\alpha \tag{2.5}$$

where (;) followed by an index indicates tensor derivative with respect to the x with that index and Ω_{ij} are the components of a symmetric covariant tensor of the second order symmetric in the indices i and j.

3. Characteristic Lines in V_n

Let e_{p_1}, $p = 1, 2, \ldots . n$ be the unit tangents to the lines of curvature in V_n. If $\mathbf{t}, \bar{\mathbf{t}}$ be any two directions in V_n, we may express $\mathbf{t}, \bar{\mathbf{t}}$ as

$$\mathbf{t} = \sum_p e_{p_1} \cos \theta_p, \tag{3.1}$$

$$\bar{\mathbf{t}} = \sum_p e_{p_1} \cos \bar{\theta}_p, \tag{3.2}$$

where θ_p, $\bar{\theta}_p$ are the angles which $\mathbf{t}$ and $\bar{\mathbf{t}}$ make with the direction e_{p1}.

The angle ϕ between $\mathbf{t}$ and $\bar{\mathbf{t}}$ is given by

$$\cos \phi = g_{ij} \sum_p e_{p_1}{}^i \cos \theta_p \sum_q e_{q_1}{}^j \cos \bar{\theta}_q$$

$$= \sum_p \cos \theta_p \cos \bar{\theta}_p, \tag{3.3}$$

since the congruences e_{p_1} $(p = 1, 2, \ldots . n)$ are mutually orthogonal.

Defining characteristic directions as a pair of conjugate (but non-asymptotic) directions, for which ϕ is extremum (so that $\cos \phi$ must also be extremum), the characteristic directions are given by those values of θ_p, $\bar{\theta}_p$ for which $\cos \phi$ is extremum, subject to the relations

$$\sum_p \cos^2 \theta_p = 1, \tag{3.4}$$

$$\sum_p \cos^2 \bar{\theta}_p = 1, \tag{3.5}$$

and

$$\Omega_{ij} \sum_p e_{p_1}{}^i \cos \theta_p \, \Sigma \, e_{q_1}{}^j \cos \bar{\theta}_q = 0$$

or

$$\Sigma \, \Omega_{ij} \, e_{p_1}{}^i e_{p_1}{}^j \cos \theta_p \cos \bar{\theta}_p = 0$$

or

$$\Sigma \, k_p \cos \theta_p \cos \bar{\theta}_p = 0 \tag{3.6}$$

where k_p is the principal curvature in the direction e_{p_1}.

Applying the Lagrange's method of undetermined multipliers, we have

$$\sum_p (\sin \theta_p \cos \bar{\theta}_p d\theta_p + \cos \theta_p \sin \bar{\theta}_p d\bar{\theta}_p)$$

$$+ \lambda \sum_p \sin \theta_p \cos \theta_p d\theta_p + \bar{\lambda} \, \Sigma \sin \bar{\theta}_p \cos \bar{\theta}_p d\bar{\theta}_p$$

$$+ \mu \sum_p (k_p \sin \theta_p \cos \bar{\theta}_p d\theta_p + k_p \cos \theta_p \sin \bar{\theta}_p d\bar{\theta}_p) = 0 \tag{3.7}$$

where λ, $\bar{\lambda}$ and μ are the Lagrange's multipliers.

Equating to zero the coefficients of the differentials $d\overline{\theta}_p$, $d\theta_p$ we have the following set of equations for the determination of λ, $\overline{\lambda}$, μ and the θ's:

$$\left.\begin{aligned} \sin\theta_p(\cos\overline{\theta}_p + \lambda\cos\theta_p + \mu k_p\cos\overline{\theta}_p) &= 0 \\ \sin\overline{\theta}_p(\cos\theta_p + \overline{\lambda}\cos\overline{\theta}_p + \mu k_p\cos\theta_p) &= 0 \end{aligned}\right\}, \qquad p = 1, 2, \ldots . n. \tag{3.8}$$

But $\sin\theta_p \neq 0$ for any value of p. For, if $\sin\theta_p = 0$ for a fixed p, we have $\cos^2\theta_q = 0$, $q \neq p$, $q = 1, 2, \ldots . n$ in which case the direction t must be a principal direction. Similarly $\sin\overline{\theta}_p \neq 0$ for any value of p.

Therefore the equations (3·8) reduce to

$$\left.\begin{aligned} \cos\overline{\theta}_p + \lambda\cos\theta_p + \mu k_p\cos\overline{\theta}_p &= 0, \\ \cos\theta_p + \overline{\lambda}\cos\overline{\theta}_p + \mu k_p\cos\theta_p &= 0 \end{aligned}\right\}, \qquad p = 1, 2, \ldots . n. \tag{3.9}$$

Multiplying the first of the equations (3·9) by $\cos\theta_p$ and the second by $\cos\overline{\theta}_p$ and summing up on p we have,

$$\left.\begin{aligned} \cos\phi + \lambda &= 0 \\ \cos\phi + \overline{\lambda} &= 0 \end{aligned}\right\}, \tag{3.10}$$

by virtue of the equations (3·3)—(3·6).

From the equations (3·10) we have

$$\lambda = \overline{\lambda} \tag{3.11}$$

Using (3·11), we may write (3·9) as

$$\begin{aligned} (1 + \mu k_p)\cos\overline{\theta}_p + \lambda\cos\theta_p &= 0 \\ (1 + \mu k_p)\cos\theta_p + \lambda\cos\overline{\theta}_p &= 0 \end{aligned} \tag{3.12}$$

For a fixed p, say $p = r$, the solutions of (3·12) are either $\cos\theta_r = 0$, $\cos\overline{\theta}_r = 0$ or else

$$(1 + \mu k_r)^2 = \lambda^2 \tag{3.13}$$

Similarly if for $p = s$, $\cos\theta_p \neq 0$, $\cos\overline{\theta}_p \neq 0$,

$$(1 + \mu k_s)^2 = \lambda^2 \tag{3.14}$$

There must exist at least two values of p, say r and s, such that $\cos \theta_p$, $\cos \overline{\theta}_p$ are different from zero; for otherwise, the directions $\mathbf{t}$ and $\overline{\mathbf{t}}$ reduce to principal directions.

Two different cases arise according as the principal curvatures are all unequal or there are sets of equal values of the principal curvatures. We shall discuss the two cases separately.

(i) *When all the curvatures are unequal.*—From (3·13) and (3·14) it is found that there cannot be more than two values of p for which $\cos \theta_p$, $\cos \overline{\theta}_p$ may be different from zero. For, we cannot have more than two consistent equations of the form (3·13) for determining λ and μ.

Thus, the characteristic directions are given by

$$\cos \theta_p = 0, \cos \overline{\theta}_p = 0, p = 1, 2, \ldots . n, \quad p \neq r, s \tag{3·15}$$

$$\left.\begin{aligned} 1 + \mu k_r &= \lambda, \\ 1 + \mu k_s &= -\lambda \end{aligned}\right\} \tag{3·16}$$

since $k_r \neq k_s$.

Using (3·16) we have from (3·12)

$$\left.\begin{aligned} \cos \theta_r + \cos \overline{\theta}_r &= 0 \\ \cos \theta_s - \cos \overline{\theta}_s &= 0 \end{aligned}\right\} \tag{3·17}$$

Also using (3·15) we have from (3·4), (3·5) and (3·6)

$$\left.\begin{aligned} \cos^2 \theta_r + \cos^2 \theta_s &= 1 \\ \cos^2 \overline{\theta}_r + \cos^2 \overline{\theta}_s &= 1 \\ k_r \cos^2 \theta_r - k_s \cos^2 \theta_s &= 0 \end{aligned}\right\} \tag{3·18}$$

From the equations (3·18) we have

$$\left.\begin{aligned} \tan^2 \theta_r = \tan^2 \overline{\theta}_r &= k_r/k_s \\ \tan^2 \theta_s = \tan^2 \overline{\theta}_s &= k_s/k_r \end{aligned}\right\} \tag{3·19}$$

(3·15) and (3·19) define a pair of real directions provided k_r, k_s, be both of the same sign, showing that corresponding to every pair of principal curvatures having the same sign we have a real pair of characteristic lines.

The angle between the characteristic lines as defined above is given by

$$\begin{aligned}\cos\phi &= \Sigma \cos\theta_p \cos\bar{\theta}_p \\ &= \cos^2\theta_s - \cos^2\theta_r \\ &= 2\cos^2\theta_s - 1 \\ &= \cos 2\theta_s = \frac{k_s - k_r}{k_s + k_r}\end{aligned} \tag{3.20}$$

The normal curvature in the characteristic direction $\mathbf{t}$ is

$$\begin{aligned}k &= k_r \cos^2\theta_r + k_s \cos^2\theta_s \\ &= \frac{2k_r k_s}{k_r + k_s}\end{aligned} \tag{3.21}$$

Similarly the normal curvature in the characteristic direction $\bar{\mathbf{t}}$ is

$$\begin{aligned}\bar{k} &= k_r \cos^2\bar{\theta}_r + k_s \cos^2\bar{\theta}_s \\ &= \frac{2k_r k_s}{k_r + k_s}\end{aligned} \tag{3.22}$$

Thus *the normal curvatures in the characteristic directions lying in the pencil determined by the principal directions* $\mathbf{e}_{r_1}$ *and* $\mathbf{e}_{s_1}$ *are equal, each being equal to the harmonic mean between the principal curvatures* $\mathbf{k}_r$ *and* $\mathbf{k}_s$.

(ii) *When there are sets of equal values of the curvature at the point.*

Let $\quad k_1 = k_2 = \ldots = k_r \neq k_s = k_{s+1} = \ldots = k_{s+q-1}$, etc.

Following the same reasoning as in case (i) we find that corresponding to two distinct values of the principal curvatures, say k_r and k_s, there exist values of p such that

$$(1 + \mu k_p)^2 = \lambda^2 \tag{3.23}$$

$$\cos\theta_p = 0, \cos\bar{\theta}_p = 0, \tag{3.24}$$

$$p = r+1, r+2, \ldots . s-1, s+q, s+q+1, \ldots . n.$$

In this case, (3.4), (3.5) and (3.6) give

$$\left.\begin{aligned}&(\cos^2\theta_1 + \cos^2\theta_2 + \ldots . + \cos^2\theta_r) \\ &\quad + (\cos^2\theta_s + \ldots . + \cos^2\theta_{s+q-1}) = \\ &(\cos^2\bar{\theta}_1 + \cos^2\bar{\theta}_2 + \ldots . + \cos^2\bar{\theta}_r) \\ &\quad + (\cos^2\bar{\theta}_s + \ldots . + \cos^2\bar{\theta}_{s+q-1}) = 1 \\ &k_r(\cos\theta_1\cos\bar{\theta}_1 + \ldots . + \cos\theta_r\cos\bar{\theta}_r) \\ &\quad + k_s(\cos\theta_s\cos\bar{\theta}_s + \ldots . \\ &\quad + \cos\theta_{s+q-1}\cos\bar{\theta}_{s+q-1}) = 0.\end{aligned}\right\} \tag{3.25}$$

From (3.23) we have

$$\left.\begin{aligned} 1+\mu k_r &= \lambda, \\ 1+\mu k_s &= -\lambda \end{aligned}\right\}, \tag{3.26}$$

giving

$$\mu = -\frac{2}{k_r+k_s}, \quad \lambda = -\frac{k_r-k_s}{k_r+k_s}. \tag{3.27}$$

(3.9) now yields

$$\cos\theta_u + \cos\bar{\theta}_u = 0, \qquad u = 1, 2, \ldots . r \tag{3.28}$$

$$\cos\theta_v - \cos\bar{\theta}_v = 0, \qquad v = s, s+1, \ldots, s+q-1. \tag{3.29}$$

Using (3.28) and (3.29), the last of the equations (3.25) becomes

$$k_r(\cos^2\theta_1 + \cos^2\theta_2 + \ldots . + \cos^2\theta_r) - k_s(\cos^2\theta_s + \ldots . + \cos^2\theta_{s+q-1}) = 0,$$

which together with the first of the equations (3.25) gives

$$\begin{aligned} &\cos^2\theta_1 + \cos^2\theta_2 + \ldots . + \cos^2\theta_r \\ &\quad = \cos^2\bar{\theta}_1 + \cos^2\bar{\theta}_2 + \ldots . + \cos^2\bar{\theta}_r = k_s/k_r + k_s, \qquad (3.30) \\ &\cos^2\theta_s + \cos^2\theta_{s+1} + \ldots . + \cos^2\theta_{s+q-1} \\ &\quad = \cos^2\bar{\theta}_s + \cos^2\bar{\theta}_{s+1} + \ldots . + \cos^2\bar{\theta}_{s+q-1} = k_r/k_r + k_s. \end{aligned}$$

(3.24) and (3.30) show that the directions $\mathbf{t}$ and $\bar{\mathbf{t}}$ are linear combinations of the directions $\frac{k_r+k_s}{k_s}\sum_{u=1}^{r} e_{u_1}\cos\theta_u$, and $\frac{k_r+k_s}{k_r}\sum_{v=s}^{s+q-1} e_{v_1}\cos\theta_v$, $\frac{k_r+k_s}{k_s}\sum_{u=1}^{r} e_{u_1}\cos\bar{\theta}_u$ and $\frac{k_r+k_s}{k_r}\sum_{v=s}^{s+q-1} e_{v_1}\cos\bar{\theta}_v$ respectively, which being linear combinations of the principal directions corresponding to equal values of curvature, are themselves principal directions.

Hence we find that *the characteristic directions are linear combinations of the principal directions corresponding to any two distinct values of the principal curvatures.*

The angle between the characteristic directions $\mathbf{t}$ and $\bar{\mathbf{t}}$ is given by

$$\cos\phi = -\lambda = \frac{k_r-k_s}{k_r+k_s}, \tag{3.31}$$

by virtue of (3.27).

The normal curvatures in the characteristic directions $\mathbf{t}$ and $\overline{\mathbf{t}}$ are

$$\begin{aligned} k &= k_r(\cos^2\theta_1 + \ldots + \cos^2\theta_r) \\ &\quad + k_s(\cos^2\theta_s + \ldots + \cos^2\theta_{s+q-1}) \\ &= 2k_rk_s/k_r + k_s. \end{aligned} \tag{3.32}$$

and

$$\begin{aligned} \overline{k} &= k_r(\cos^2\overline{\theta}_1 + \ldots + \cos^2\overline{\theta}_r) \\ &\quad + k_s(\cos^2\overline{\theta}_s + \ldots + \cos^2\overline{\theta}_{s+q-1}) \\ &= 2k_rk_s/k_r + k_s, \end{aligned} \tag{3.33}$$

by virtue of (3.30)

Relations (3.31)–(3.33) are the same as (3.20)–(3.22).

4. Directions for which the Ratio of the Geodesic Torsion (or Second Curvature) and the Normal Curvature is Extremum

The geodesic torsion in the direction $\mathbf{t} = \sum_p e_{p_1}\cos\theta_p$ is given by (Manikarnikamma, 1952).

$$\tau_g^2 = \tfrac{1}{2}\sum_{p=1}^{n}\sum_{q=1}^{n}\cos^2\theta_p\cos^2\theta_q(k_p - k_q)^2 \tag{4.1}$$

The normal curvature in the direction of $\mathbf{t}$ is

$$k_n = \sum_{p=1}^{n} k_p\cos^2\theta_p \tag{4.2}$$

The directions for which τ_g/k_n is extremum are the same as those for τ_g^2/k_n^2 is extremum, (for τ_g is zero only in a principal direction).
Now,

$$\begin{aligned} \tau_g^2/k_n^2 &= (\tau_g^2 + k_n^2)\,k_n^{-2} - 1 \\ &= \sum_p k_p^2\cos^2\theta_p\left(\sum_p k_p\cos^2\theta_p\right)^{-2} - 1. \end{aligned} \tag{4.3}$$

The directions for which τ_g/k_n is extremum are therefore given by

$$\left.\begin{aligned} &\sum_{p=1}^{n}\frac{\partial}{\partial\theta_p}\left[\frac{\sum_1^n k_r^2\cos^2\theta_r}{\left(\sum_1^n k_r\cos^2\theta_r\right)^2} - 1\right] = 0, \\ &\sum_{p=1}^{n}\cos^2\theta_p = 1, \\ \text{and} \\ &\sum_{p=1}^{n}\cos\theta_p\sin\theta_p\,d\theta_p = 0. \end{aligned}\right\} \tag{4.4}$$

The first of the equations (4.4) may be written as

$$\sum_p [k_p^2 \cos\theta_p \sin\theta_p (\Sigma k_r \cos^2\theta_r)^2$$

$$-2(\Sigma k_r \cos^2\theta_r) k_p \cos\theta_p \sin\theta_p \Sigma k_r^2 \cos^2\theta_r] d\theta_p = 0 \quad (4.5)$$

Applying the Lagrange's method of undetermined multipliers we have,

$$\left(\sum_1^n k_r \cos^2\theta_r\right) k_p^2 \cos\theta_p \sin\theta_p - 2k_p \cos\theta_p \sin\theta_p \Sigma k_r^2 \cos^2\theta_r$$

$$+ \lambda \cos\theta_p \sin\theta_p = 0, \quad (4.6)$$

$$(p = 1, 2, \ldots . n)$$

where λ is the Lagrange's multiplier.

Now $\sin\theta_p \neq 0$ for any p, for otherwise the direction **t** must be a principal direction. (4.6) therefore gives

$$\cos\theta_p \left[k_p^2 \sum_1^n k_r \cos^2\theta_r - 2k_p \sum_1^n k_r^2 \cos^2\theta_r + \lambda\right] = 0 \quad (4.7)$$

$$(p = 1, 2, \ldots . n)$$

(4·7) gives either (i) $\text{Cos}\,\theta_p = 0$,

or (ii) $k_p^2 \sum_1^n k_r \cos^2\theta_r - 2k_p \sum_1^n k_r^2 \cos^2\theta_r + \lambda = 0.$

As in §3 two different cases arise:

CASE (i). *When all the principal curvatures are unequal.*

Since **t** is not a principal direction, there must exist at least two values of p, say r and s, such that $\cos\theta_p = 0$, *i.e.*, for at least two values of p,

$$k_p^2 \sum_1^n k_p \cos^2\theta_p - 2k_p \sum_1^n k_p^2 \cos^2\theta_p + \lambda = 0 \quad (4.8)$$

Putting $p = r, s$ in (4.8) and subtracting we have

$$(k_r + k_s) \sum_1^n k_p \cos^2\theta_p - 2\sum_1^n k_p^2 \cos^2\theta_p = 0 \quad (4.9)$$

since $$k_r \neq k_s.$$

Multiplying (4.8) throughout by $\cos^2\theta_p$ and summing up on p we have

$$\lambda = \sum_1^n k_p^2 \cos^2\theta_p \sum_1^n k_p \cos^2\theta_p \quad (4.10)$$

From (4.9) it follows that there cannot exist more than two values of p such that $\cos\theta_p$ may be different from zero; for, if r, s, w be three such values, we have as in (4.9)

$$\left.\begin{aligned}(k_r + k_w)\sum_1^n k_p \cos^2\theta_p - 2\sum_1^n k_p^2 \cos^2\theta_p = 0\\ (k_s + k_w)\sum_1^n k_p \cos^2\theta_p - 2\sum_1^n k_p^2 \cos^2\theta_p = 0\end{aligned}\right\} \quad (4.11)$$

By subtracting the equations in (4.11) we find that either $k_r = k_s$ or else

$$\sum_1^n k_p \cos^2\theta_p = 0,$$

i.e., direction of **t** must be asymptotic. Since none of these alternatives is possible, we find that

$$\cos\theta_p = 0,\ p = 1, 2, \ldots . n, p \neq r, s, \quad (4.12)$$

$$\left.\begin{aligned}k_r^2 \sum_1^n k_p \cos^2\theta_p - 2k_r \sum_1^n k_p^2 \cos^2\theta_p + \lambda = 0\\ k_s^2 \sum_1^n k_p \cos^2\theta_p - 2k_s \sum_1^n k_p^2 \cos^2\theta_p + \lambda = 0\end{aligned}\right\} \quad (4.13)$$

The second of the equations (4.4) now gives

$$\cos^2\theta_r + \cos^2\theta_s = 1 \quad (4.14)$$

Using (4.12), (4.9) gives

$$\left.\begin{aligned}\tan^2\theta_r = k_r/k_s,\\ \tan^2\theta_s = k_s/k_r.\end{aligned}\right\} \quad (4.15)$$

(4.12), (4.15) and (4.16) define a pair of real directions corresponding to every pair of distinct values of principal curvatures of the same sign.

CASE (ii). *When there are sets of equal values of principal curvatures at any point.*

Let $k_1 = k_2 = \ldots . = k_r \neq k_s = k_{s+1} = \ldots . = k_{s+q-1}$, etc.

Proceeding as in § 3 above, we can show that the directions for which the ratio of geodesic torsion to normal curvature is extremum are given by

$$\cos\theta_p = 0, p \neq 1, 2, \ldots . r, s, s+1, \ldots . s+q-1, \quad (4.16)$$

$$\left.\begin{aligned}\cos^2\theta_1 + \cos^2\theta_2 + \ldots . + \cos^2\theta_r = \frac{k_r}{k_r + k_s}\\ \cos^2\theta_s + \cos^2\theta_{s+1} + \ldots . + \cos^2\theta_{s+q-1} = \frac{k_s}{k_r + k_s}\end{aligned}\right\} \quad (4.17)$$

Comparing (4.12), (4·15), (4.16) and (4.17) with (3.15), (3.19), (3.24) and (3.30) respectively we find that *the directions for which the ratio of the geodesic torsion and normal curvature is an extremum are characteristic directions,*

and are, as such, linear combinations of the principal directions corresponding to two distinct values of the principal curvatures.

5. PARTICULAR CASE

If the enveloping space be an Euclidean 3-space, we find from §4 above the known result (Mishra, 1947), that the *characteristic lines on a surface are the directions for which the ratio of geodesic torsion and the normal curvature is an extremum.*

6. SUMMARY

Upon a surface of positive Gaussian curvature there exists a unique conjugate system for which the angle between the directions at any point is the minimum angle between the conjugate directions at that point. This system of lines is called characteristic lines. In the present paper characteristic lines of a hypersurface V_n imbedded in a Riemannian V_{n+1} have been studied. It has been proved that characteristic directions are linear combinations of the principal directions corresponding to any two distinct values of the principal curvatures. It has also been proved that the normal curvatures in the two characteristic directions lying in the pencil determined by the principal directions corresponding to two distinct values of the principal curvatures are equal, each being equal to the harmonic mean between the principal curvatures. The directions for which the ratio of the geodesic torsion and normal curvature is an extremum have also been studied and it has been shown that the directions for which the ratio of the geodesic torsion and the normal curvatures is an extremum are characteristic directions.

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SPECTRUM OF AXI-SYMMETRIC TURBULENCE IN A CONTRACTING STREAM

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1. Introduction

Batchelor[1] considered the passage of isotropic turbulence in a 'sudden' contraction. The condition 'sudden' ensures that the problem is a linear one and tractable.

Further extensions were made in solving this problem by Ribner and Tucker.[2] They considered the spectra and the turbulence levels at points upstream and downstream of a contraction and derived the relations between the various quantities. Thus, if the initial spectra and turbulence levels in a sudden contraction are known and if the conditions are isotropic, the final spectral forms as well as the turbulence levels can be determined. If it is assumed that the contraction is axi-symmetric and the mean velocity ratio is l_1, we have from considerations of continuity

$$\sigma l_1 l_2 l_3 = 1, \tag{1.1}$$

where $\sigma = 1$, for incompressible flows and $l_2 = l_3$ for axi-symmetry. Ribner and Tucker have determined the form of the spectral tensor at a point B downstream of the contraction in terms of the spectral tensor at point A upstream, assuming that the decay is negligible. Thus, if $\Gamma_{\alpha\beta}{}^{A}(\kappa)$ is the spectrum tensor at the point A, where κ is the wave number vector,

$$\Gamma_{\alpha\beta}{}^{B}(\kappa) = \frac{l_1 l_2^2}{l_\alpha l_\beta}\left[\Gamma_{\alpha\beta}{}^{A}(\kappa) + \frac{(\Gamma_{\alpha 1}\kappa_\beta + \Gamma_{1\beta}\kappa_\alpha)\,\kappa_1(1-\epsilon)}{\epsilon\kappa_1^2 + \kappa_2^2 + \kappa_3^2} + \right.$$
$$\left. + \frac{\Gamma_{11}{}^{A}\kappa_1^2\kappa_\alpha\kappa_\beta\,(1-\epsilon)^2}{(\epsilon\kappa_1^2 + \kappa_2^2 + \kappa_3^2)^2}\right]. \tag{1.2}$$

Here, $\epsilon = l_2^2/l_1^2$ and $\epsilon \ll 1$ for large l_1 and

$$\kappa_1, \kappa_2, \kappa_3 = l_1 K_1, l_2 K_2, l_3 K_3. \tag{1.3}$$

(1.2) is the basic equation for us. This equation has been used by Ribner and Tucker, to obtain many results, assuming initial isotropy. In the following lines, we shall use the same equation to solve the more difficult problem of

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initial axi-symmetry. In a wind tunnel, or other apparatus, where most of the aeronautical experiments are done, the geometry would suggest that, by and large, one encounters axi-symmetric turbulence rather than isotropic turbulence.

2. The Initial Form of the Axi-symmetric Tensor

The general form of axi-symmetric tensor has been given by Batchelor, as

$$\phi_{ij}(\kappa, \lambda) = A\kappa_i\kappa_j + B\lambda_i\lambda_j + C\delta_{ij} + D\kappa_i\lambda_j + E\kappa_j\lambda_i, \tag{2.1}$$

where A, B, C, D and E are the defining scalars and functions of κ^2 and $\kappa_i\lambda_i$.

For the spectral tensor $\Gamma_{\alpha\beta}(\kappa, \lambda)$:

$$\left.\begin{aligned} &\kappa_\alpha \Gamma_{\alpha\beta} = \kappa_\beta \Gamma_{\alpha\beta} = 0 \\ &\Gamma_{\alpha\beta}(\kappa, \lambda) = \Gamma_{\beta\alpha}(\kappa, \lambda) \end{aligned}\right\} \tag{2.2}$$

Following Proudman and Reid,[3] we define the operators

$$\Delta_\alpha{}^i = \delta_{\alpha i} - \frac{\kappa_\alpha\kappa_i}{\kappa^2}; \quad \Delta_\beta{}^j = \delta_{\beta j} - \frac{\kappa_\beta\kappa_j}{\kappa^2}. \tag{2.3}$$

Then the general axi-symmetric tensor which is solenoidal in both indices α and β is given by

$$\begin{aligned} \Gamma_{\alpha\beta}(\kappa, \lambda) &= \Delta_\alpha{}^i(\kappa)\,\Delta_\beta{}^j(\kappa)\,\phi_{ij}(\kappa, \lambda) \\ &= B\left(\lambda_\alpha - \frac{\kappa_\alpha\kappa_i\kappa_i}{\kappa^2}\right)\left(\lambda_\beta - \frac{\kappa_\beta\kappa_j\kappa_j}{\kappa^2}\right) \\ &\quad + C\left(\delta_{\alpha j} - \frac{\kappa_\alpha\kappa_j}{\kappa^2}\right)\left(\delta_{\beta j} - \frac{\kappa_\beta\kappa_j}{\kappa^2}\right), \end{aligned} \tag{2.4}$$

where B and C are the defining scalars, which are functions of κ^2 and $\kappa_i\lambda_i$. Instead of B and C we write Γ_2 and Γ_1 for the defining scalars and rewrite the general spectrum tensor in the form:

$$\begin{aligned} \Gamma_{\alpha\beta}(\kappa, \lambda) &= \Gamma_1\left(\delta_{\alpha j} - \frac{\kappa_\alpha\kappa_j}{\kappa^2}\right)\left(\delta_{\beta j} - \frac{\kappa_\beta\kappa_j}{\kappa^2}\right) + \\ &\quad + \Gamma_2\left(\lambda_\alpha - \frac{\kappa_\alpha\kappa_i\lambda_i}{\kappa^2}\right)\left(\lambda_\beta - \frac{\kappa_\beta\kappa_j\lambda_j}{\kappa^2}\right). \end{aligned} \tag{2.4 a}$$

Equation (2.4 *a*) has to be used in conjunction with equation (1.2) to obtain the form of the spectral tensor downstream of the contraction in our case.

The evaluation of the integrals becomes very difficult as the defining scalars are functions of κ^2 and $\kappa_i\lambda_i$ in this case. Whereas in the case of isotropic turbulence, which was dealt by the preceding workers, the defining scalar is simple, as there is no preferred direction.

The diagonal terms of the tensor, given by (2·4 *a*), at the initial section A are:

$$\left.\begin{aligned} \Gamma_{11}^{A}(\kappa, \lambda) &= \Gamma_1\left(1-\frac{\kappa_1^2}{\kappa^2}\right)+\Gamma_2\left(1-\frac{\kappa_1^2}{\kappa^2}\right)^2 \\ \Gamma_{22}^{A}(\kappa, \lambda) &= \Gamma_1\left(1-\frac{\kappa_2^2}{\kappa^2}\right)+\Gamma_2\frac{\kappa_2^2\kappa_1^2}{\kappa^4} \\ \Gamma_{33}^{A}(\kappa, \lambda) &= \Gamma_1\left(1-\frac{\kappa_3^2}{\kappa^2}\right)+\Gamma_2\frac{\kappa_3^2\kappa_1^2}{\kappa^4}. \end{aligned}\right\} \tag{2.5}$$

The other three terms of the tensor can also be evaluated and will be mentioned later.

3. Spectral Forms Downstream of the Contraction

The form of the spectral tensor at the section B could be obtained by introducing the corresponding equations in (1·2), for the terms at the section A. Thus,

$$\Gamma_{11}^{B}(K, \lambda)=\frac{l_1 l_2^2}{l_1^2}\,\Gamma_{11}^{A}(\kappa)\,\frac{\kappa^4}{(\epsilon\kappa_1^2+\kappa_2^2+\kappa_3^2)^2}, \tag{3.1 a}$$

where Γ_{11}^{A} [we will hereafter write $\Gamma_{\alpha\beta}^{A}$ instead of $\Gamma_{\alpha\beta}^{A}(\kappa, \lambda)$ as there will be no confusion] is given by the first line of equation (2·5). Hence, we obtain

$$\Gamma_{11}^{B}(K, \lambda)=\frac{l_2^2\left[\Gamma_1\left(1-\frac{\kappa_1^2}{\kappa^2}\right)+\Gamma_2\left(1-\frac{\kappa_1^2}{\kappa^2}\right)^2\right]\kappa^4}{l_1(\epsilon\kappa_1^2+\kappa_2^2+\kappa_3^2)^2}. \tag{3.1}$$

Similarly, we get

$$\Gamma_{22}^{B}(\mathrm{K}, \lambda)=l_1\left[\Gamma_{22}^{A}+\frac{2\Gamma_{12}^{A}\kappa_2\kappa_1(1-\epsilon)}{\epsilon\kappa_1^2+\kappa_2^2+\kappa_3^2}+\right.$$
$$\left.+\frac{\Gamma_{11}^{A}\kappa_1^2\kappa_2^2(1-\epsilon)^2}{(\epsilon\kappa_1^2+\kappa_2^2+\kappa_3^2)^2}\right], \tag{3.2 a}$$

where Γ_{11}^{A} and Γ_{22}^{A} are given in equation (2.5) and

$$\Gamma_{12}^{A}(\kappa, \lambda)=-\frac{\kappa_2\kappa_1}{\kappa^2}\left[\Gamma_1+\Gamma_2\left(1-\frac{\kappa_1^2}{\kappa^2}\right)\right]. \tag{3.3}$$

Hence equation (3.2), similar to (3.1), can be obtained by substituting the values of Γ_{11}^{A}, Γ_{12}^{A}, Γ_{22}^{A} from equations (2.5) and (3.3) in (3.2 *a*).

We can, in a similar fashion, obtain the value of $\Gamma_{33}^{B}(\mathrm{K}, \lambda)$ from (3.2 *a*) by substituting Γ_{33}^{A}, Γ_{13}^{A} and κ_3 instead of Γ_{22}^{A}, Γ_{13}^{A} and κ_2; also it can be derived directly from (1·2) and (2.4 *a*).

4. Determination of the Correlation Tensor

The relation, between the correlation and the spectrum tensors, can be expressed by the following equations:

$$\left.\begin{aligned} R_{\alpha\beta}{}^{A}(r) &= \int\int\int_{-\infty}^{+\infty} \Gamma_{\alpha\beta}{}^{A}(\kappa)\, e^{-i\kappa\cdot r}\, d\tau(\kappa) \\ R_{\alpha\beta}{}^{B}(r) &= \int\int\int_{-\infty}^{+\infty} \Gamma_{\alpha\beta}{}^{B}(K)\, e^{-iK\cdot r}\, d\tau(K). \end{aligned}\right\} \tag{4.1}$$

The auto-correlation at the point is further given by

$$\left.\begin{aligned} R_{\alpha\alpha}{}^{A}(0) &= \int\int\int_{-\infty}^{+\infty} \Gamma_{\alpha\alpha}{}^{A}(\kappa)\, d\tau(\kappa) \\ R_{\alpha\alpha}{}^{B}(0) &= \int\int\int_{-\infty}^{+\infty} \Gamma_{\alpha\alpha}{}^{B}(K)\, d\tau(K). \end{aligned}\right\} \tag{4.2}$$

So, we have got a method of determining the auto-correlations of the turbulent fluctuations at the point B downstream of the contraction, if we know the spectrum at a point A upstream of the contraction.

5. Evaluation of $\overline{u_\alpha{}^2}$

The turbulent fluctuations at a point are designated u, v and w as usual, then we have the following relationships:

$$\overline{u_A{}^2} = R_{11}{}^{A}(0);\quad \overline{v_A{}^2} = R_{22}{}^{A}(0);\quad \overline{w_A{}^2} = R_{33}{}^{A}(0) \tag{5.1}$$

$$\overline{u_B{}^2} = R_{11}{}^{B}(0);\quad \overline{v_B{}^2} = R_{22}{}^{B}(0);\quad \overline{w_B{}^2} = R_{33}{}^{B}(0). \tag{5.2}$$

For convenience, in integration, we use spherical polar co-ordinates:

$$\left.\begin{aligned} \kappa_1 &= \kappa\cos\theta \\ \kappa_2 &= \kappa\sin\theta\cos\phi \\ \kappa_3 &= \kappa\sin\theta\sin\phi \\ d\tau(\kappa) &= \kappa^2\sin\theta\, d\theta\, d\phi\, d\kappa \\ d\tau(K) &= \frac{k^2}{l_1 l_2 l_3}\sin\theta\, d\theta\, d\phi\, d\kappa. \end{aligned}\right\} \tag{5.3}$$

We shall now try to evaluate the individual mean squares of the turbulent fluctuations.

(*a*) *Variation of* $\overline{u^2}$

We have from (5.1) and (4.2), for the section A:

$$\overline{u_A{}^2} = \int\int\int_{-\infty}^{+\infty} \Gamma_{11}{}^{A}(\kappa)\, d\tau(\kappa), \tag{5.4}$$

where

$$\Gamma_{11}^{A}(\kappa, \lambda) = \Gamma_1 \sin^2\theta + \Gamma_2 \sin^4\theta \tag{5.4 a}$$

from the first line of (2.5), by introducing the values given by (5.3).

Similarly, we obtain from (5.2) and (4.2), the value of $\overline{u_B^2}$ as

$$\overline{u_B^2} = \int_{-\infty}^{+\infty}\int\int \Gamma_{11}^{B}(K)\, d\tau(K), \tag{5.5}$$

where

$$\Gamma_{11}^{B}(K, \lambda) = \frac{l_2^2}{l_1^2}\,\frac{(\Gamma_1 \sin^2\theta + \Gamma_2 \sin^4\theta)}{(\epsilon\cos^2\theta + \sin^2\theta)^2}. \tag{5.5 a}$$

Hence, we have

$$\frac{\overline{u_B^2}}{\overline{u_A^2}} = \frac{\int_{-\infty}^{+\infty}\int\int \Gamma_{11}^{B}(K)\, d\tau(K)}{\int_{-\infty}^{+\infty}\int\int \Gamma_{11}^{A}(\kappa)\, d\tau(\kappa)}. \tag{5.6}$$

(*b*) *Variation of* $\overline{v^2}$

From the second equation (5.1) and the first line of (4.2), we obtain the value of $\overline{v_A^2}$, as:

$$\overline{v_A^2} = \int_{-\infty}^{+\infty}\int\int \Gamma_{22}^{A}(\kappa)\, d\tau(\kappa), \tag{5.7}$$

where

$$\Gamma_{22}^{A}(\kappa, \lambda) = \Gamma_1(1-\sin^2\theta\cos^2\phi) + \Gamma_2 \sin^2\theta\cos^2\theta\cos^2\phi. \tag{5.7 a}$$

For the section B, $\overline{v_B^2}$ is obtained by using equations (5.2) and (4.2), as

$$\overline{v_B^2} = \int_{-\infty}^{+\infty}\int\int \Gamma_{22}^{B}(K)\, d\tau(K), \tag{5.8}$$

where

$$\Gamma_{22}^{B}(K, \lambda) = l_1\Big[\Gamma_1(1-\sin^2\theta\cos^2\phi) + \Gamma_2 \sin^2\theta\cos^2\theta\cos^2\phi - \frac{2\sin^2\theta\cos^2\theta\cos^2\phi\,(1-\epsilon)\,(\Gamma_1 + \Gamma_2\sin^2\theta)}{\epsilon\cos^2\theta + \sin^2\theta} + \frac{\sin^2\theta\cos^2\theta\cos^2\phi\,(1-\epsilon)^2\,(\Gamma_1\sin^2\theta + \Gamma_2\sin^4\theta)}{(\epsilon\cos^2\theta + \sin^2\theta)^2}\Big] \tag{5.8 a}$$

Hence,

$$\frac{\overline{v_B^2}}{\overline{v_A^2}} = \frac{\int_{-\infty}^{+\infty}\int\int \Gamma_{22}^{B}(K)\, d\tau(K)}{\int_{-\infty}^{+\infty}\int\int \Gamma_{22}^{A}(\kappa)\, d\tau(\kappa)}. \tag{5.9}$$

(*c*) *Variation of* $\overline{w^2}$

The value of $\overline{w^2}$ is obtained at sections A and B in a manner similar to the calculation of $\overline{v^2}$, for this purpose we have to use Γ_{33} in place of Γ_{22}. Hence

$$\frac{\overline{w_B^2}}{\overline{w_A^2}} = \frac{\int\int\int_{-\infty}^{+\infty} \Gamma_{33}^{B}(K)\, d\tau(K)}{\int\int\int_{-\infty}^{+\infty} \Gamma_{33}^{A}(\kappa)\, d\tau(\kappa)}. \tag{5.10}$$

6. EVALUATION OF THE INTEGRALS IN EXPRESSIONS FOR $\overline{u_a^2}$

The general problem of the evaluation of the integrals (5.4) – (5.10), is very difficult as the defining scalars Γ_1 and Γ_2 are functions of κ^2 and $\kappa_i\lambda_i$. Also the forms of these functions are not known. *But we can evaluate those integrals under the initial assumption that* Γ_1 *and* Γ_2 *are only functions of* κ, *and obtain a specialised picture of the flow.* In the following lines, we shall discuss the results under this assumption.

(*a*) *Variation of* $\overline{u^2}$

The integral expression (5.4), can be solved with the aid of (5.4 *a*), resulting in

$$\overline{u_A^2} = \frac{8\pi}{3}\left(\Phi_1 + \frac{4}{5}\Phi_2\right), \tag{6.1}$$

where, we have put

$$\Phi_1 = \int_0^\infty \Gamma_1 \kappa^2 d\kappa; \quad \Phi_2 = \int_0^\infty \Gamma_2 \kappa^2 d\kappa. \tag{6.1 a}$$

When, (5.5 *a*) is introduced in (5.5) the integral becomes

$$\overline{u_B^2} = \frac{2\pi}{l_1^2}\left[\Phi_1 I_1^{(1)} + \Phi_2 I_2^{(1)}\right], \tag{6.2}$$

where,

$$\left.\begin{aligned} I_1^{(1)} &= \left[\frac{-1}{1-\epsilon} + \frac{2-\epsilon}{(1-\epsilon)^{3/2}} \operatorname{arc\,tanh}\ \sqrt{1-\epsilon}\right] \\ I_2^{(1)} &= \frac{2+\epsilon}{(1-\epsilon)^2} - \frac{\epsilon(4-\epsilon)}{(1-\epsilon)^{5/2}} \operatorname{arc\,tanh}\ \sqrt{1-\epsilon}. \end{aligned}\right\} \tag{6.2 a}$$

Hence, we get for (5·6):

$$\frac{\overline{u_B^2}}{\overline{u_A^2}} = \frac{3}{4l_1^2}\left[\frac{\Phi_1 I_1^{(1)} + \Phi_2 I_2^{(1)}}{\Phi_1 + \frac{4}{5}\Phi_2}\right]. \tag{6.3}$$

(*b*) *Variation of* $\overline{v^2}$

Expression (5.7) can be evaluated by introducing in it the value of Γ_{22}^{A} from (5.7 *a*), leading to

$$\overline{v_A^2} = \frac{8\pi}{3}\left(\Phi_1 + \frac{1}{10}\Phi_2\right). \tag{6.4}$$

Similarly, equation (5.5) can be solved and simplified to:

$$\overline{v_B^2} = \frac{\pi}{l_2^2}\left[\Phi_1 I_1^{(2)} + \Phi_2 I_2^{(2)}\right], \tag{6.5}$$

where

$$I_1^{(2)} = \frac{2-\epsilon}{1-\epsilon} - \frac{\epsilon^2}{(1-\epsilon)^{3/2}} \text{ arc tanh } \sqrt{1-\epsilon}$$

$$I_2^{(2)} = \frac{-2\epsilon^2}{(1-\epsilon)^2} + \frac{\epsilon^2(2+\epsilon)}{(1-\epsilon)^{5/2}} \text{ arc tanh } \sqrt{1-\epsilon} \tag{8.5 a}$$

Hence, equation (5.9) becomes:

$$\frac{\overline{v_B^2}}{\overline{v_A^2}} = \frac{3}{8l_2^2}\left[\frac{\Phi_1 I_1^{(2)} + \Phi_2 I_2^{(2)}}{\Phi_1 + \frac{1}{10}\Phi_2}\right]. \tag{6.6}$$

(*c*) *Variation of* $\overline{w^2}$

$\overline{w^2}$ varies in the same way as $\overline{v^2}$ because of axi-symmetry and we can write the expression (5.10) as:

$$\frac{\overline{w_B^2}}{\overline{w_A^2}} = \frac{3}{8l_2^2}\left[\frac{\Phi_1 I_1^{(3)} + \Phi_2 I_2^{(3)}}{\Phi_1 + \frac{1}{10}\Phi_2}\right], \tag{6.7}$$

where the quantities $I_1^{(3)}$ and $I_2^{(3)}$ are given in the same way as in (6.5 *a*).

We would like to emphasize the fact that expressions (6.3), (6.6) and (6.7) are true only if Γ_1 and Γ_2 are only functions of κ, but they would not hold, if they are functions of κ^2 and $\kappa_i\lambda_i$ in a general way. There is no way of predicting this, unless experiments are made and the spectra evaluated in the case of axi-symmetric turbulence.

7. One-Dimensional Longitudinal Spectrum

If we make a Fourier analysis of the variation of velocity along a line, the spectrum functions can be obtained by integrating over all κ for the lateral components. Thus, the contribution to the mean square velocity

component $\overline{u_\alpha^2}$ [which is equal to $R_{\alpha\alpha}(0)$], in the x_1-direction, from all the wave numbers between $|\kappa_1|$ and $|\kappa_1| + |d\kappa_1|$ is

$$\Theta_\alpha(\kappa_1)\, d\kappa_1 = \left[2 \int_{-\infty}^{+\infty}\int \Gamma_{\alpha\alpha}\, d\kappa_2\, d\kappa_3\right] d\kappa_1$$

or

$$\Theta_\alpha(\kappa_1) = 2 \int_{-\infty}^{+\infty}\int \Gamma_{\alpha\alpha}\, d\kappa_2\, d\kappa_3 \tag{7.1}$$

which yields $\Theta_1^A(\kappa_1)$ or $\Theta_1^B(\kappa_1)$ according as we use Γ_{11}^A or Γ_{11}^B, in place of $\Gamma_{\alpha\alpha}$ in the integration of the R.H.S.

Θ_1 is called the one-dimensional longitudinal spectrum of the flow turbulence. Similarly, we can obtain the lateral spectra when $\alpha = 2, 3$ in terms of the scalar functions Γ_1 and Γ_2, which define the axi-symmetric turbulence tensor.

8. Concluding Remarks

Just as we carried out the calculations in paragraph 4, we can also determine the one-dimensional spectral functions, under the assumption that Γ_1 and Γ_2 are functions of only κ. But, since no purpose is served unless we are sure of the functional dependence of Γ_1 and Γ_2 on κ^2 and $\kappa_i\lambda_i$, we do not want to take the trouble to solve (7.1). But the problem has been stated and once the forms of the defining scalars are determined, by experiment* or otherwise, the calculation becomes straightforward, though laborious.

It is intended to tackle the non-linear problem of a contraction, which is not sudden, in a subsequent paper.

9. Summary

The passage of axi-symmetric turbulence in a suddenly contracting stream has been investigated. A form of axi-symmetric tensor suitable for this study has been derived. Assuming that the form of turbulence is initially axi-symmetric, upstream of the contraction, the spectral forms downstream have been given. The ratio of the turbulence levels, on either side of the contraction, has been evaluated in integral form. Further, the integrals have been solved, assuming that the defining scalars are functions only of the wave number κ. The method of evaluating one-dimensional spectra has been indicated. The whole investigation is based on the linearised approach.

*Note: Dr. Mahinder S.Uberoi of the University of Michigan, U.S.A., wrote to the author, while the latter was at the Johns Hopkins University in July 1955, that he was carrying on some experiments relative to the problem treated in this paper.

10. Nomenclature

u	turbulent fluctuation.
x	co-ordinates.
l_1	mean velocity ratio.
l_2, l_3	vertical and lateral contraction ratios.
κ	wave number vector.
σ	compressibility factor ($\sigma = 1$, for incompressible flows).
Γ	spectral tensor.
R	correlation tensor.
A, B	sections upstream and downstream, respectively, of the contraction.
1, 2, 3; α, β, γ	subscripts for denoting directions.
Γ_1, Γ_2	defining scalars.

$\epsilon = l_2^2/l_1^2$.

Other symbols are defined in the text, as and when they appear for the first time.

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THE IONIC CHARACTER OF SINGLY BONDED MOLECULES

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Abstract

The overlap factors for bond electrons in various diatomic halides are calculated making use of a simple relation where the overlap factor is an inverse exponential function of the difference between the two atomic radii of the molecule concerned. These overlap factors together with the hybridization values of 15 percent for Cl, and 10 percent for Br and I are used to calculate the ionic characters for various diatomic molecules from the values of the nuclear quadrupole coupling constants obtained by earlier workers. These ionic characters are then plotted against electronegativity differences and the points are found to be fairly well represented by a smooth curve. It is shown that this curve can in general be used for the determination of the ionic characters in the halogen containing single bonds of certain polyatomic molecules. The quadrupole coupling constants are calculated from the ionic characters obtained from the curve and are compared with those observed. The effects of the distortion of the closed shells and of the neighbouring ions on eQq are discussed.

Introduction

The purpose of this paper is to discuss the method of obtaining the ionic character in halide molecules in gas phase from the nuclear quadrupole coupling constants.[1, 2] These coupling constants which are obtained from the quadrupole hyperfine structure are denoted by eQq, where e represents the electronic charge, Q is the nuclear quadrupole moment and $q \equiv \left(\frac{\partial^2 V}{\partial z^2}\right)$ is the gradient of the electric field at the nucleus due to extranuclear charges and depends primarly on the electrons in the p orbit of the valence shell; z is the co-ordinate along the symmetry or bond axis.

The quadrupole coupling constant for a halogen atom forming a hybrid bond with a negative ionic character of amount β, is given by[3]

$$eQq_{\text{molecule}} = (-1 + s - d - S^2)(1 - \beta)\, eQq_{\text{Atom}} \qquad (1)$$

where s and d represent the respective contributions of the corresponding electrons in the bonding orbital of the halogen atom which is given by

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$$\Psi_{\text{Halogen}} = (1 - s - d)^{\frac{1}{2}} \Psi_p \pm s^{\frac{1}{2}} \Psi_s \pm d^{\frac{1}{2}} \Psi_d$$

S represents the overlap factor $\int \Psi_A \Psi_B^* d\tau$ for two atoms A and B of the diatomic molecule, and eQq_{Atom} is obtainable from atomic data.[4]

Since it is very hard to distinguish quantitatively the effects of s character from those due to d character, it is not necessary to retain separate symbols for them as in (1), and one may use the symbol α for the combination $(s - d)$.

If the bond is positively ionic that is when the halogen ion is positive, two electrons are missing from the valence shell of the halogen atom, and therefore the number of unbalanced p electrons will increase to 2, giving rise to a gradient[5] of the electric field equal to $2q^+$. Here q^+ represents the gradient of the electric field due to one valence p electron when the atom is positively ionic, and is somewhat greater than the corresponding 'q' when the atom is neutral. This is because the interaction between a valence p electron and the nucleus is somewhat larger in this case than in the case of the neutral atom. The ratio of q^+ and q is taken as $(1 + \epsilon)$, where ϵ is nearly 0·25 for most atoms.[3] Hence the eQq of a halide molecule for a positive ionic state will be given by $-2(1 + \epsilon)\, eQq_{\text{Atom}}$, where the hybridization has been neglected because of the increase of promotional energy required. Therefore, the quadrupole coupling constant for an atom with a positive ionic character of amount β is given by

$$eQq_{\text{mol.}} = [(-1 + \alpha - S^2)(1 - \beta) - 2(1 + \epsilon)\beta]\, eQq_{\text{Atom}} \qquad (2)$$

The exact value of β can be obtained from (1) and (2) if the values of α and S^2 are known. Gordy[6, 7] assumes that both α and S^2 are negligible, but the following difficulties arise with such an assumption:—

(1) The ionic characters for FCl and FBr with such an assumption come out to be about 26 percent and 33 percent respectively* from equation (2), whereas from Gordy's graph[7] they should be about 50 percent and 60 percent respectively. Gordy says that this inconsistency could be avoided if one assumes hybridization in Cl and Br atoms of FCl and FBr in the positive ionic state. To explain this inconsistency one has to assume the hybridization for positive ionic importance to be 31 percent and 28 percent in FCl and FBr respectively,† as the hybridization has to be taken as negligible for covalent importance according to his views. This seems to be improbable.

* From Gordy's formula (21) (ref. 7) the values of ionic character come out to be 28 percent and 35 percent for FCl and FBr respectively.

† If Gordy's assumption is correct, formula (2) has to be rewritten as

$$eQq_{\text{mol.}} = -[(1 - \beta) + 2(1 + \epsilon - \alpha)\beta]\, eQq_{\text{Atom}}$$

If β for FCl and FBr has to come out as 50 percent and 60 percent respectively from this formula, α has to be taken as 31 percent. and 28 percent respectively.

(2) The ionic character for BrCl molecule considering the coupling constant for Cl nucleus comes out to be 5·6 percent, whereas it comes out to be 12 percent while considering Br nucleus.

(3) Gordy[7] points out that in obtaining ionic characters for diatomic molecules from dipole moment data, one need not find it necessary to take hybridization into account, which he says is in support of his assumption that hybridization is negligible. But one should remember that the hybridization effect on nuclear quadrupole coupling constant is different from that on molecular dipole moment. Moreover, the effects of hybridization of the two atoms in a diatomic molecule act in opposite directions for dipole moment considerations.

Dailey and Townes[3] took α into consideration and neglected S^2, because no satisfactory calculations of the overlap effects seemed feasible. They followed a simple rule that the halogen bonds have 15 percent s character whenever the halogen is bonded to an atom which is more electropositive than the halogen by as much as 0·25 unit, and 0 percent otherwise. If one generalizes this rule and makes it applicable to Cl in BrCl where Br is more electropositive than Cl by 0·2 units, the value of β neglecting S^2 comes out to be negative which does not have a physical meaning. It is probably for this reason that they restricted 15 percent hybridization to cases where the halogen under consideration is more electronegative than the bonding atom by more than 0·25 unit.

The hybridization in a positively ionic state is suppressed due to increase of promotional energy and therefore it may be assumed to be 0 percent for the positively ionic importance only. But Dailey and Townes[3] assumed 0 percent hybridization even for covalent importance‡ in their calculations on FCl, FBr, etc., all of which have only partial ionic character.

In this present paper both α and S^2 will be taken into consideration. The values of α and S^2 will be based on certain general assumptions keeping the physical ideas in mind, as it would be difficult to obtain these values more precisely. In this paper the assumptions of Dailey and Townes[3] regarding hybridization will be modified, so that the difficulties pointed out above will not arise. Further the modified assumptions could also be extended to the case of polyatomic molecules.

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‡ This they do giving the reason that if the resonance energy between the covalent and ionic states is to be maximum, it is necessary that both states possess the same amount of hybridization. If this reason is correct the hybridization has to be taken as something between 0 and 15 percent and certainly not 0 percent because in the molecule considered, the covalent character is more predominant than the positive ionic character.

Assumptions Regarding Overlapping and Hybridization

(*a*) *Overlapping in diatomic molecules*:—Overlapping is essentially a measure of the amount of interpenetration of the bond-electron distributions of the two atoms,[8] and has a finite value whenever a bond exists between the two atoms. Thus one can start with the assumption that the overlap factor S is a decreasing function of either R_{ab} or $|r_a - r_b|$, where R_{ab} represents the distance between the two nuclei, and r_a and r_b represent the radii of the two atoms forming a diatomic molecule. Now using the atomic radii given by Slater[10] and assuming $R_{ab} = (r_a + r_b)$, the overlap factors for various homopolar molecules are obtained from the tables given by Mulliken *et al.*,[10] and are given in Table I. Here only those molecules in which the atoms have one electron in the outermost orbit of ground state

Table I

Overlap Factors in Homopolar Molecules

	Molecule		Overlap factor	R_{ab} in A	$\lvert r_a - r_b \rvert$ in A
1.	I_2	..	0·407	2·24	0
2.	Cl_2	..	0·385	1·92	0
3.	Al_2	..	0·385	2·74	0
4.	Na_2	..	0·375	4·34	0
5.	F_2	..	0·320	0·82	0
6.	B_2	..	0·320	1·64	0
7.	Li_2	..	0·456	3·26	0
8.	H_2	..	(0·586)	1·06	0

were considered and it was assumed that the overlapping takes place only between these two electrons which are also assumed to form the covalent bond.

This table (I) shows that the variations of S with R_{ab} are small, and the values in different homopolar molecules are fairly constant. Thus it appears that S can be more correctly represented by a function of $|r_a - r_b|$ than by that of R_{ab}. Therefore assuming that S becomes negligible as $|r_a - r_b|$ becomes extremely large, a simple functional form of S^2 is

$$S^2 = Ae^{-2(|r_a - r_b|)} \qquad (3)$$

where A is a constant. The value of this parameter A is found to be 0·21 from the coupling data for BrCl, taking the ionic character β to be 6 percent,[11] and assuming α for Cl in this molecule to be 15 percent.[3, 12] This value of A introduced in (3) yields $S = 0{\cdot}45$ for a homopolar molecule in fairly good agreement with the average value of S from Table I.

(*b*) *Hybridization.*—When the bond is purely covalent, α for the halogen atom in question arises due to the mixing of the valence *p* orbital with the *s* or *d* orbitals of the same atom. It will be fairly correct to assume that for the *covalent importance* the α for a particular halogen atom has the same value in various molecules of the same halogen, but may have different values for different halogens; for example, α for Br and I will probably be smaller than for Cl, because the *d* character in α for Br and I is greater than that for Cl.

The promotional energy required for positively ionic state of the atom will be increased and hence the hybridization is reduced, so that it can be assumed that for this positively ionic importance the hybridization is suppressed to 0.

Considering Cl in ICl and assuming 15 percent α for Cl, the ionic character in the molecule was found to be 21 percent. Now considering the iodine atom in ICl and keeping β as 21 percent the value of α for I is found to be 9 percent. An approximate round figure of 10 percent will therefore be taken as the value of α for I in different molecules. Following a similar procedure the value of α for Br in different molecules is taken as 10 percent.

Incidentally it may be mentioned that the above assumptions would enable one to predict the eQq in the molecules I_2, Br_2 and Cl_2 in gaseous phase to be $-$ 2420 mc., 811 mc. and $-$ 109·5 mc. respectively.*

CALCULATIONS OF IONIC CHARACTERS IN DIATOMIC HALIDES

The values of S^2 have been calculated for a number of diatomic molecules from (3) using the atomic radii given by Slater,[9] and are included in Table II. Using these values of S^2, and assuming α for Cl to be 15 percent and that for

* These values of eQq for these homopolar molecules are calculated from the equation

$$eQq_{\text{mol.}} = -(1-\alpha)\left(2 - \frac{1}{1+S^2}\right) eQq_{\text{Atom}}$$

which, when S^2 is small, reduces to the equations (1) and (2), where β is to be taken as 0 for homopolar molecules.

The eQq in gas phase for these molecules are not observed so far but the corresponding observed values[1] in solid state are $-$ 2153 mc., 765 mc. and $-$ 108·95 mc. for I_2, Br_2 and Cl_2 respectively.

Br and I to be 10 percent, the ionic characters for the various molecules have been calculated from (1) and (2), and are also given in Table II. These values of the ionic character obtained are plotted against the electronegativity differences ($| x_a - x_b |$), and the shape of the resulting curve is shown in Fig. 1. The values of ($| x_a - x_b |$) used for all except TlCl are those given by Huggins.[13] Since Huggins has not given the value of electronegativity for Tl, the corresponding value calculated by Gordy[6] from a force constant relation has been used.

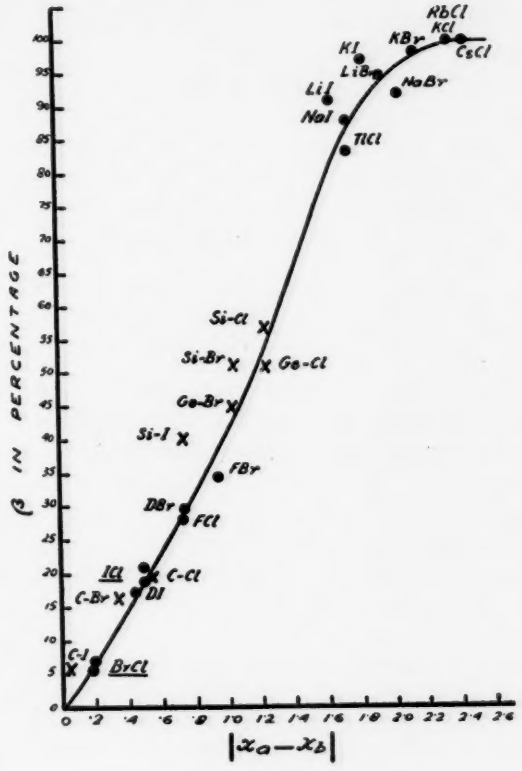

FIG. 1

IONIC CHARACTER IN ALKALI HALIDES

From equation (1) one expects that the magnitude of the quadrupole coupling constant for halides molecules should decrease asymptotically towards zero with the increase of ionic character which in turn is an increasing function of $| x_a - x_b |$. On the other hand as the electronegativity difference

increases the quadrupole coupling constant in the chloride molecules, as shown in Table II, decreases in magnitude up to KCl where it changes its sign and increases in magnitude from KCl to CsCl. This change in alkali chlorides can be explained in the following manner:—

The contributions to q in molecules[14] come from,

(*a*) the valence electrons associated with the atom under consideration,

(*b*) the neighbouring ions and atoms, and

(*c*) the distortions of non-bonding closed shells of electrons around the nucleus in question,

of which the first is the most predominant. If D represents the effect on quadrupole coupling constant due to distortions of the closed shells around the halogen nucleus, and i represents the effect due to presence of adjacent ions or atoms, the equations (1) and (2) for coupling constants can be more precisely rewritten as

$$eQq_{\text{mol.}} = [(-1 + \alpha - S^2)(1 - \beta) + (D - i)\beta]\, eQq_{\text{Atom}}$$
(negatively ionic state) (4)

$$eQq_{\text{mol}} = [(-1 + \alpha - S^2)(1 - \beta) - 2(1 + \epsilon)\beta - (D - i)\beta]\, eQq_{\text{Atom}}$$
(positively ionic state) (5)

From (4) it is clear that when β approaches 1, the term $(D - i)\beta\, eQq_{\text{Atom}}$ becomes appreciable and will be responsible for the change in sign of the quadrupole coupling constant if the distortion effects are greater than those of adjacent ions. This explains the change in sign of eQq for KCl and its increase in magnitude from then on up to CsCl. The best values of β as obtained from the curve in Fig. 1 are 99·5 percent for KCl and RbCl and 100 percent for CsCl. With these values of β the factor $(D - i)\beta\, eQq_{\text{Atom}}$ can be calculated to be equal to 0·44 mc. for KCl, 1·24 mc. for RbCl and 3·00 mc. for CsCl. As $\beta \approx 1$ here, this shows that $(D - i)$ is increasing with the increase in interionic distance, which is quite understandable as the term i decreases rapidly with the increase in interionic distance. The presence of the factor $(D - i)$ in (4) explains why quadrupole coupling constants as calculated from the simple formula (1) for alkali halides come out to be higher in general than those observed.

It is interesting to see that, in the case of FBr where Br is partially positively ionic and where the ionic character is about 40 percent the quadrupole coupling constant as calculated from (2) comes out to be also higher than that observed. This is understandable from (5) which is applicable to FBr if the factor $(D - i)$ is taken as negative. This would mean that the effect

TABLE II

Ionic Characters and eQq for Diatomic Halides in Gaseous Phase

TABLE II

Ionic Characters and eQq for Diatomic Halides in Gaseous Phase

Molecule		[a] Hybr. in %	$\lvert r_a - r_b \rvert$ in A (Slater)	S^2	β Calc in %	β from graph in %	$\lvert x_a - x_b \rvert$ (Huggins)	Obs. eQq in mc.	Calc. eQq in mc. using β from graph	Ref.
Cl^{35}	..	..	..	..	..	..	..	−109·74	..	*a*
BrCl	..	15	0·18	0·150	6·0	6·5	0·20	−103·6	−102·6	*b*
ICl	..	15	0·34	0·106	21·4	19	0·50	− 82·5	−85·0	*c*
FCl	..	15	0·37	0·100	28·5	30	0·75	−146·0	−148·5	*d*
TlCl	..	15	1·10	0·023	83·5	86	1·75[6]	−15·8	−13·4	*e*
TCl	..	15	0·25	0·127	38·0	39	0·95	−67·0	−65·3	*j*
KCl	..	15	2·54	0·001	100	99·5	2·35	0·04	−0·4	*b*
RbCl	..	15	3·08	0·000	100	99·5	2·35	0·774	−0·47	*f*
CsCl	..	15	3·47	0·000	100	100	2·45	3·0	0·0	*f*
Br^{79}	..	..	..	..	..	..	..	769·76	..	*a*
BrCl	..	10	0·18	0·150	7	6·5	0·20	876·8	869·2	*b*
FBr	..	10	0·55	0·070	34·5	39	0·95	1089·0	1125·0	*i*
DBr	..	10	0·43	0·089	30	30	0·75	533·0	533·0	*g*
LiBr	..	10	0·67	0·053	95	94	1·95	37·2	43·8	*f*
NaBr	..	10	1·21	0·019	92	96·5	2·05	58·0	28·3	*f*
KBr	..	10	2·36	0·002	98·5	98	2·15	10·244	13·8	*f*
I^{127}	..	..	..	..	..	..	..	−2292·84	..	*a*
ICl	..	10	0·34	0·106	19	19	0·50	−2944	−2944	*c*
DI	..	10	0·59	0·064	17·5	17	0·45	−1823	−1835	*h*
LiI	..	10	0·51	0·076	91	81	1·65	−198	−415	*f*
NaI	..	10	1·05	0·026	88	86·5	1·75	−259·87	−287·0	*f*
KI	..	10	2·20	0·0025	97	91	1·85	−60·0	−184·2	*f*

a See *ref.* 4.
b Smith, Sidewell and Williams, *Phys. Rev.*, 1950, **79**, 1007.
c Townes, Merritt and Wright, *Ibid.*, 1948, **73**, 1334.
d Gilbert, Roberts and Griswold, *Ibid.*, 1949, **76**, 1723.
e Lee, Carlson, Fabricand and Rabi, *Ibid.*, 1950, **78**, 340.
f See ref. 11.
g Gordy, W. and Burrus, C. A., *Ibid.* (to be published).
h Burrus, C. A. and Gordy, W., *Ibid.* (to be published).
i Smith, Tidwell and Williams, *Ibid.*, 1950, **77**, 420.
j Burrus, Gordy, Benjamin and Livingston, *Phys. Rev.*, 1955, **97**, 1661.

of the neighbouring ion in the ionic state of the molecule is larger than the distortion effect, whereas it is smaller in alkali halides, which is reasonable because the interionic distance in FBr is much smaller than that in any alkali halide. It is to be pointed out that the effect of the term $(D - i)$ is also noticeable in FCl in a similar way as in FBr but in a smaller degree as β for the former is smaller than for the latter. From the deviations between the observed and calculated values of eQq, it can be estimated that the effect of the term $(D - i)$ in the ionic states of FCl and FBr is to decrease the quadrupole coupling constant by about 8 percent and 12 percent respectively. Thus the combined effect of neighbouring ions and of the distortion of closed shells is in general to decrease the eQq in diatomic molecules.

IONIC CHARACTER IN POLYATOMIC MOLECULES OF HALOGENS

The ionic characters for the single bonds containing halogens in various polyatomic molecules have been calculated from (1) neglecting the overlap effect† and the corresponding values obtained are given in Table III. These values are plotted in Fig. 1 and are marked with cross ($\times$). It is interesting to see that all the points in general fit in fairly well with the curve drawn for the diatomic halides.

In the case of polyatomic molecules, the effect of the involved double bond character[15, 16] on eQq should be taken into consideration besides the other effects discussed for diatomic halides. In this paper we are, however, considering molecules involving a small percentage of double bond character only. The effect of the double bond character is to increase eQq,[16] but the combined effect of the distortion of closed shells and the neighbouring ions as mentioned earlier is to decrease eQq. The fact that the ionic characters calculated from (1) fit in general with the curve in Fig. 1 shows that the effect of the double bond character is approximately compensated by that of the term $(D - i)$. Therefore, it appears that the ionic character for a single

† Considering a molecule like H_3C-Cl one can see that because the carbon atom for covalent importance forms single bonds with each of the other four atoms of the molecule, the atomic orbital Ψ_{3p_σ} of Cl will have certain possibilities of overlap with each of the bonding orbitals Ψ_{2s}, $\Psi_{2p_{\pm\pi}}$ and Ψ_{2p_σ} of carbon. These possible overlap factors are proportional to

$$\int \Psi_{2s} \Psi^*_{3p_\sigma} d\tau, \int \Psi_{2p_{\pm\pi}} \Psi^*_{3p_\sigma} d\tau \text{ and } \int \Psi_{2p_\sigma} \Psi^*_{3p_\sigma} d\tau.$$

But

$$\int \Psi_{2s} \Psi^*_{3p_\sigma} d\tau \approx 1/\sqrt{3} \int \Psi_{2p_\sigma} \Psi^*_{3p_\sigma} d\tau^{(8)} \text{ and } \int \Psi_{2p_{\pm\pi}} \Psi^*_{3p_\sigma} d\tau$$

can be shown to be zero. Thus the average value of the overlap integral for the C-Cl bond is small compared with $\int \Psi_{2p_\sigma} \Psi^*_{3p_\sigma} d\tau$ which usually represents the overlap factor for a diatomic molecule. S^2 may therefore be neglected for approximate purposes in such kind of polyatomic molecules as considered in this paper.

TABLE III

Ionic Characters and eQq *for Polyatomic Molecules in Gaseous Phase*

Molecule	Hybrid-ization	Ionic Character calculated in %	Ionic Character in % from graph	$\lvert x_a - x_b \rvert$ (Huggins)	Observed *eQq* in mc.	Calculated *eQq* in mc.	Ref.
Cl^{35} ..	..	..	..	..	−109·74	..	..
CH_3C-Cl ..	15	19·5	21	0·55	−75·3	−73·7	*a, b*
CH_3Si-Cl ..	15	57	54·5	1·25	−40·0	−42·4	*d*
CH_3Ge-Cl ..	15	51	54·5	1·25	−46·0	−42·4	*g*
Cl^{37} ..	..	..	..	..	769·76	..	..
CH_3C-Br ..	10	16·5	13	0·35	577·3	602·7	*a, c*
CH_3Si-Br ..	10	51·5	44	1·05	336·0	388·0	*e*
CH_3Ge-Br ..	10	45	44	1·05	380·0	388·0	*h*
Br^{81} ..	..	..	..	..	−2292·84	..	..
CH_3C-I ..	10	6	1·5	0·05	−1934	−2032	*a*
CH_3Si-I ..	10	40	30	0·75	−1240	−1448	*f*

a Gordy, Simmons and Smith, *Phys. Rev.*, 1948, **74,** 243.
b Karplus R. and Sharbaugh, *Ibid.*, 1949, **75,** 889, erratum 1449.
c Sharbaugh, A. H. and Mattern, J., *Ibid.*, 1949, **75,** 1102.
d Sharbaugh, A. H., *Ibid.*, 1948, **74,** 1870.
e Sharbaugh, Bragg, Madison and Thomas, *Ibid.*, 1949, **76,** 1419.
f Sharbaugh, Heath Thomas and Sheridan, *Nature*, 1953, **171,** 87.
g Dailey, Mays and Townes, *Phys. Rev.*, 1949, **76,** 136.
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bond involving a halogen atom in a polyatomic molecule can be approximately obtained from the curve drawn for diatomic halides. The ionic characters obtained by this procedure are given in Table IV for the single

TABLE IV

Calculated Ionic Characters and eQq *for Certain Polyatomic Molecules, the* eQq *for which is not so far observed in the Gaseous Phase*

Molecule	Ionic Character in percentage from graph	*eQq* in mc. calculated for gas phase	*eQq* in mc. observed in solid state	Ref.
$SnCl_4$ ..	54·5	−42·4	−48·2	*a*
PCl_3 ..	41	−55·0	−52·3	*a*
$AsCl_3$ ..	44	−52·4	−50·5	*a*
$SbCl_3$ ..	46	−50·4	−40·2	*a*
SnI_4 ..	30	−1448	−1363	*b*

a Livingston, R., See ref. 1, p. 366.
b Dehmelt, H. G., *Naturwiss.*, 1950, **37,** 398.

bonds in different polyatomic molecules along with the corresponding calculated eQq. As the coupling constants for these molecules in the gaseous phase are not yet known, those observed for the molecules in solid phase are included in the table for comparison.

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COMPARATIVE STUDIES OF ALTERNATING AND DIRECT CURRENT POLAROGRAPHY: EFFECT OF pH

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Analysis of a mixture of two or more electro-oxidisable or reducible substances with their characteristic half-wave potentials, in a given supporting electrolyte, close to each other, cannot be carried out on the conventional direct current polarography; thus a mixture of Cd^{++} and In^{+++} which have their half-wave potentials as $-0{\cdot}610$ and $-0{\cdot}565$ volts *vs.* S.C.E. could not be analysed on dc. polarography.[1] This appeared to be a limitation to the polarographic work using dc. potentials. This difficulty could, however, be overcome by using alternating current polarography in which a known ac. voltage was superimposed over the dc. potentials fed to the dropping mercury electrode (d.m.e.) and the alternating current passing through the system was measured as a function of the applied dc. potential[2]; these studies led to the observation of well-defined peaks due to the reversible reduction or oxidation, at d.m.e., of the substances, with their summits occurring at the potentials corresponding to the characteristic half-wave potentials recorded on dc. polarography and with the peak or summit current being proportional to the concentrations of the electro-active substances.[1, 2] A significant feature of these studies was that the alternating polarograms were remarkably sharp in the sense that the potential width of the waves was small, at low superimposed ac. voltages, say 5–10 millivolts (500 cycles/sec.), which led to the possibility of the analysis of the mixture containing Cd^{++} and In^{+++}.[1] Further, comparative studies of the potential-widths of the dc. and ac. polarograms obtained at different concentrations of the electro-active substance also revealed that the alternating current polarography had remarkable advantage over the dc. polarography to the effect that by using low concentrations the former can be suitably employed for analysis of mixtures of two components with their half-wave potentials close to each other.[3] These studies have now been extended to the investigation of the effect of pH on the wave-widths of ac. and dc. polarograms of cadmium, on which no data exist in the literature.

EXPERIMENTAL

The apparatus and the electric circuit employed have been described in the previous communication.[3]

The dropping mercury electrode had the following characteristics: at a pressure of 32 cm. of mercury, drop time (t) was 1·6 secs. in 0·1 M KCl solution with open circuit; and the weight of mercury dropping per sec. (m) was 2·5 mg.

In the alternating current polarography, 30 millivolts (50 cycles/sec.) was used, throughout the present series of experiments, as the superimposed ac. voltage.

Cadmium sulphate used was Merck sample and was recrystallised several times in twice distilled water and later dried at 160° C.

The pH of the solution of Cd^{++} of a fixed concentration was altered by using citrate buffers. Potassium citrate used for this purpose was of B.D.H. quality; hydrochloric acid and sodium hydroxide employed were Merck

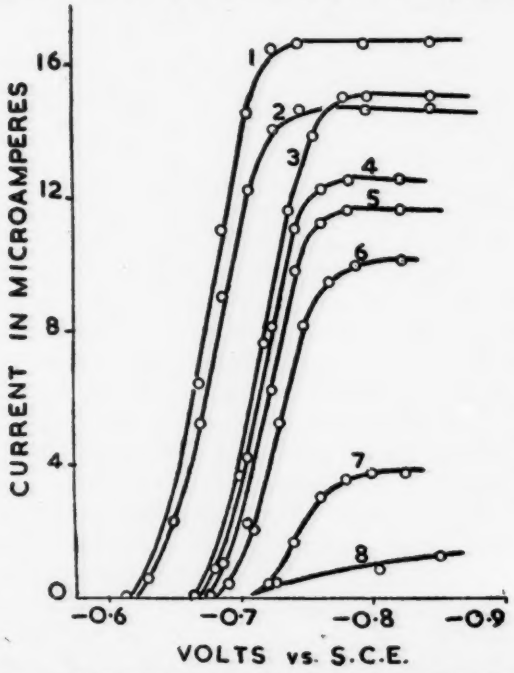

FIG. 1. D.C. polarograms of Cd^{++} at different pH values. Curves 1 to 8 refer to pH values 4 to 11 respectively.

analysed samples. Required quantities of citrate and hydrochloric acid or sodium hydroxide solutions were mixed in the manner described by Meits[4] and others, with cadmium solution to give a sample of desired pH; the mixtures were so prepared that the final solution was of the same volume and contained fixed quantities of Cd^{++} and citrate. The pH of the solution was measured by a Beckmann pH meter.

Results and Discussion

Figure 1 gives a typical series of dc. polarograms of Cd^{++} at different pH values; these data refer to a concentration of 2 mM of Cd^{++} and of 0·5 M of Cit.--- The corresponding ac. polarograms are returned in Figs. 2 (*a*) and 2 (*b*). It was interesting to note that at all pH values below 10, Cd^{++} gave

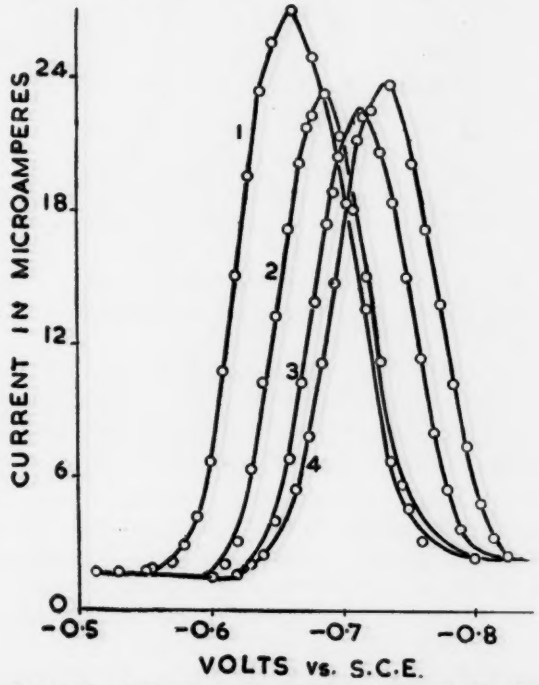

Fig. 2 (*a*). A.C. polarograms of Cd^{++} at different pH values. Curves 1 to 4 refer to pH values 4 to 7 respectively.

thermodynamically reversible waves on dc. polarography (Fig. 1) and well-defined peaks on ac. polarography (Fig. 2). At pH values greater than 10, however, no wave could be observed (Fig. 1) indicating that no reversible

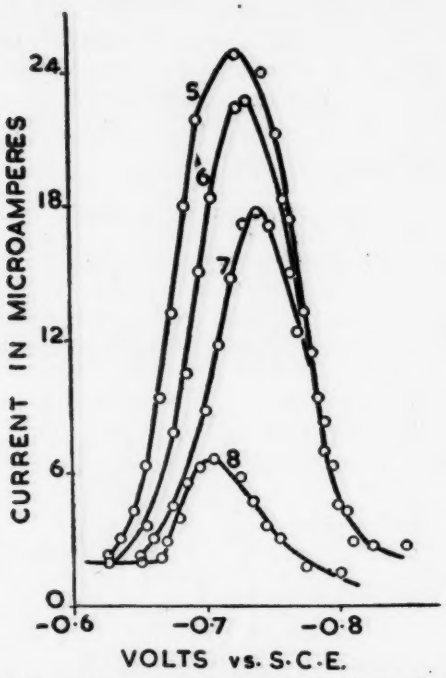

FIG. 2 (*b*). A.C. polarograms of Cd^{++} at different pH values. Curves 5 to 8 refer to pH values 8 to 11.

reduction of Cd^{++} occurred at the dropping mercury electrode[4]; similar results were recorded on the alternating current polarography. This observation suggested a convenient method for eliminating the interference of Cd^{++} in alternating and direct current polarographic determination of other substances.[4]

Further, at pH values below 10, the diffusion current i_d of the dc. polarograms, as well as the summit current i_s of the ac. polarograms depended markedly upon the pH of the solution. Fig. 3 gives the variation of i_d and i_s with pH. It was interesting to note that i_d and i_s decreased initially with increase of pH from 1–5. Thus i_d was 26, 20 and 14 μ amps. at pH values 1, 3 and 5 respectively (Curve 1, Fig. 3). At the pH values between 5–7, i_d and i_s remained constant with pH. With further increase of pH above 8, both i_d and i_s decreased sharply (see Fig. 3). These features indicated that at varied ranges of pH, different characteristic equilibria leading to the existence of thermodynamically reversible complexes of cadmium and citrate ions, were in operation. This was substantiated by the variation of half-wave

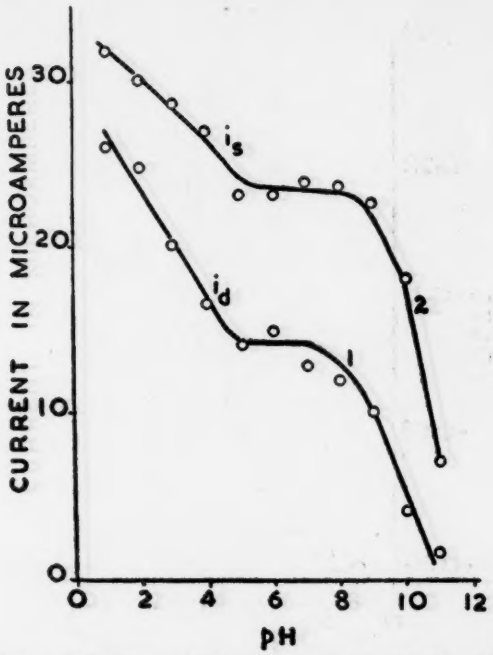

FIG. 3. Variation of diffusion and the summit current with pH of the solution.

potential ($E_{\frac{1}{4}}$) of the dc. polarograms and the summit potential (E_s) of the ac. polarograms, with the pH of the solution; these data are shown graphically in Fig. 4. It was interesting to note that at all pH values investigated, $E_{\frac{1}{4}}$ and E_s were roughly the same as evidenced by the observation that the points representing $E_{\frac{1}{4}}$ and E_s at varied pH fell roughly on the same curve (Fig. 4). Further, $E_{\frac{1}{4}}$ and E_s increased with pH. In the region of pH values between 5-7 the rate of increase of $E_{\frac{1}{4}}$ and E_s was less than that recorded at pH values between 1–5; again at pH > 8, the rate of variation of $E_{\frac{1}{4}}$ and E_s with pH was considerably enhanced. The following processes appear to be occurrent in the corresponding pH ranges:

(1) $Cd^{++} + Cit.^{---} \rightleftharpoons Cd\ Cit.^{-} + 2e$ (pH < 5)

(2) $Cd^{++} + H\ Cit.^{--} \rightleftharpoons (Complex) + H^{+}$ (pH $\approx 5-7$)

(3) $Cd\ Cit.^{-} + OH^{-} \rightleftharpoons Cd\ (OH)\ Cit.^{--}$ (pH > 7)

Enough evidence in support of these has been adduced by Meits,[4] Lingane[5] and others[6–8]; the values of the corresponding equilibrium constants[4] have been evaluated; and these are: $K_1 = 6\times10^{-5}$, $K_2 = 5\times10^{+1}$ and $K_3 = 9\times10^{-6}$.

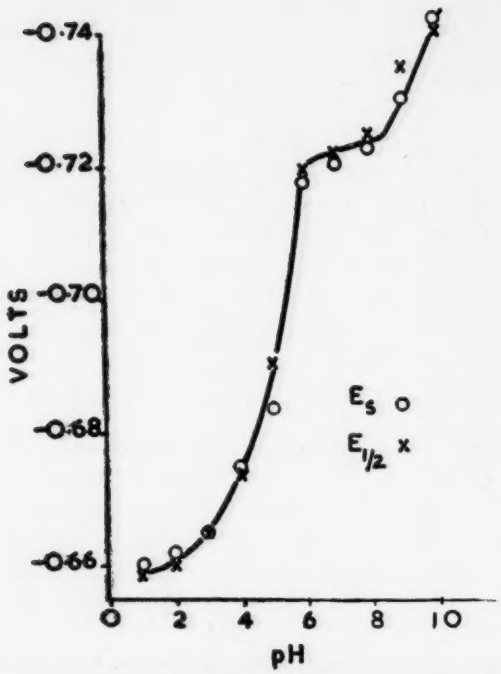

FIG. 4. Effect of pH on the half-wave and summit potentials of Cd^{++}.

The data in Fig. 5 show the variation of the potential-width of the dc. and ac. polarograms returned in Figs. 1 and 2. As indicated in the previous

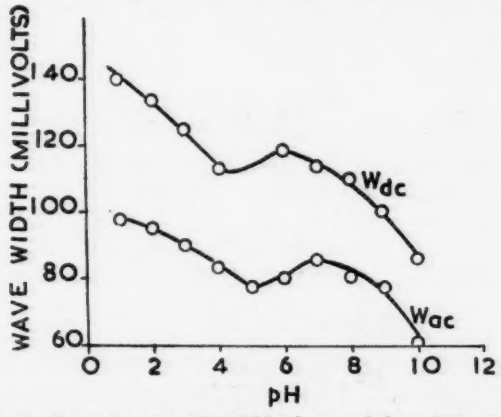

FIG. 5. Effect of pH on the potential width of ac. and dc. polarograms of Cd^{++}.

communication[3] the wave-spread of the ac. peaks was taken as the potential-width of the polarograms corresponding to the current values equal to half the summit current. It was interesting to note that in the entire range of the pH values studied, the wave-spread of the ac. polarograms (W_{ac}) was less than that corresponding to the dc. polarograms (W_{dc}). Thus, *e.g.*, at pH = 2, the dc. polargorams spread over a potential region of 140 millivolts while the ac. waves occurred over 98 millivolts; similarly at pH = 10, W_{dc} and W_{ac} were 85 and 60 millivolts respectively. The difference between the wave-widths of ac. and dc. polarograms was maximum at low pH values. These data indicate that analysis of a mixture containing Cd^{++} as one of the components can be carried satisfactorily on ac. polarography in the pH range 5–6 where the current values are appreciable and the wave-width is considerably smaller than in dc. polarography.

Summary

Alternating and direct current polarograms of cadmium were recorded at different pH values in the range 1–12. At pH < 11, cadmium was reduced reversibly at the dropping mercury electrode, giving well-defined waves on both ac. and dc. polarography. The wave-width of ac. polarograms was less than that of dc. polarograms in the entire range of pH studied.

Acknowledgement

Authors' thanks are due to Professor K. S. G. Doss, D.Sc., F.R.I.C., F.A.Sc., F.Inst.P., Director, Indian Institute of Sugar Technology, for his interest in the work, and to the Ministry of Education, Government of India, for a maintenance grant to one of us (S. K. D. A.).

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SPECTROPHOTOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANTS OF 4-(*p*-NITROPHENYL-AZO)-8-HYDROXY-QUINOLINE*

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Azo dyes have been employed extensively as analytical reagents for metal ions. Gutzeit and Monnier[1,2] studied a large number of azo dyes containing the oxine nucleus and concluded that they gave specific tests for Hg^{++}, Pd^{++}, Ni^{++}, etc. Bogel Desering and Shreve[3] estimated the relative values of the azo dyes as analytical reagents for the varied metal ions. Of these azo dyes, 4-(*p*-nitrophenyl-azo)-8-hydroxy-quinoline in alcoholic medium appeared to be important as an analytical reagent expecially for Ca^{++}.[4,5] During an examination of its applicability to the estimation, with ease, of calcium content in sugarcane juices it appeared desirable to determine the dissociation constant(s) of the dye, the knowledge of which is of marked importance for clear understanding the use of the dye in analytical work. No data on this aspect exist in the literature. The present communication reports the determination of the dissociation constant(s) by employing the characteristic absorption spectra of the substance in the visible region.

Experimental

The starting material employed by the authors for the preparation of the azo dye were acetanilide and 8-hydroxy-quinoline; and these were of the following quality: 8-hydroxy-quinoline used was of B.D.H. quality. Acetanilide was a Bush product; and was converted into *p*-nitroaniline in the usual manner[6]; this last was purified by recrystallisation in rectified spirit till it gave a constant melting point 147·5° (148°) C. *p*-nitroaniline (1 mol.) was dissolved in N-HCl acid (2½ mol.). The solution was cooled to 5° C. and then treated with 10% solution of $NaNO_2$ (1 mol.). The diazotised solution was added dropwise to alkaline solution of 8-hydroxy-quinoline (2½ mol. in N-NaOH) maintained at 5° C.; the reaction mixture was stirred for one hour to ensure complete coupling.[5] The dye was then precipitated by acidifying it with 2 N acetic acid; filtered and washed several times with water. It was crystallised 4-5 times in rectified spirit; a product with a melting point of 258° C. was obtained.

* A preliminary note was published in *Naturwiss.*, 1956, **43**, 179.

The absorption spectra of the alcoholic solution of the azo dye at different pH values was studied with a Unicam S.P. 350 D.G. Spectrophotometer; this had one cm. effective light path. The buffers used were due to Clark and Lubs and to Sörensen[7]; the actual pH of the solution (1 vol. of solution + 1 vol. of buffer) was checked by a Beckmann pH meter.

Results and Discussions

Figure 1 gives a typical series of results on the absorption spectra of 4-(*p*-nitrophenyl-azo)-8-hydroxy-quinoline in alcoholic solution at different pH in the range 4–12. These data refer to a concentration of 0·002 mM of the azo

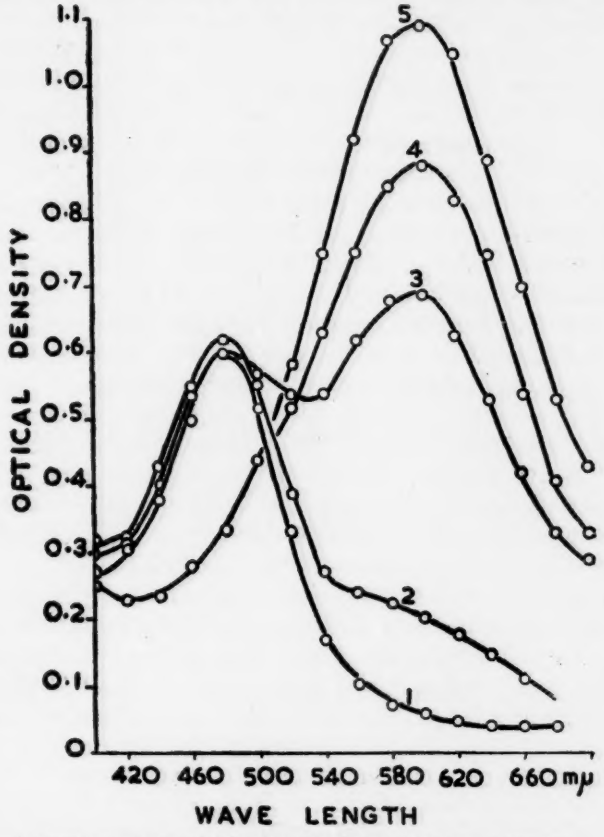
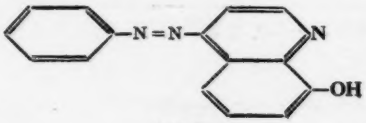


Fig. 1. Absorption spectra of 4-(*p*-nitrophenyl-azo)-8-hydroxy-quinoline.

Curve 1 refers to pH=6; 2 to pH=7·0; 3 to pH=8·0; 4 to pH=8·2 and 5 to pH=10·5 12·0.

dye. It was interesting to note that the dye exhibited absorption maximum at $\lambda = 600$ mμ in alkaline solution and another maximum at $\lambda = 480$ mμ in the neutral and acidic solutions. It is to be remarked that freshly prepared solution of the dye exhibited an absorption maximum at 560 mμ in alkaline solutions, which on long standing, however, shifted permanently to 600 mμ. The experiments were conducted only when the system exhibited stable and perfectly reproducible characteristics.

It was interesting to observe that, while the absorption at $\lambda = 480$ mμ was not affected appreciably, the same at $\lambda = 600$ mμ was, however, variant markedly with the change of the pH of the solution especially in the range 5–12 pH. The system exhibited an isobestic point, though not well defined in character, in the neighbourhood of $\lambda = 510$ mμ (Fig. 1). The data in Fig. 2 show the variation of the optical density of the system at $\lambda = 600$ mμ with pH of the solution. It was interesting to note that at $\lambda = 600$ mμ the optical density was almost unaltered with pH from 4–6·5; and a further change in pH from 6·5–7, increases the optical density markedly. Thus, *e.g.*, optical density was 0·05, 0·08 and 0·2 at pH = 6·0, 6·5 and 7·5 respectively. Later in the pH range 7·5 and 8, the optical density of the system did not vary appreciably; in fact, it tended to saturate in the sense that the curve representing the variation of optical density with pH appeared to run parallel to the pH axis (see Fig. 2). Further increase of pH again increased optical density, which was unaffected by pH > 9·0 (see Fig. 2). Thus there appeared to exist two inflexions in the curve representing the variation of optical density with pH of the solution, indicating that 4-(*p*-nitrophenyl)-8-hydroxy-quinoline possess two dissociation constants. The data given in Fig. 2 are therefore not amenable for the familiar calculations, from spectrophotometric data, of the dissociation constant of the substance, which take into consideration that the optical density at different hydrogen concentrations is dependent on the proportion of the substance in the acid or base form (molecule or ion). The present circumstance is apparently complicated as in the case of the calculation of the dissociation constant of a dibasic acid by potentiometric titration method.[7] The existence of two dissociation processes in the system under investigation is presumably due to the presence of the -OH and $\geqslant$ N in the molecule of the dye (NQOH)



(NQOH)

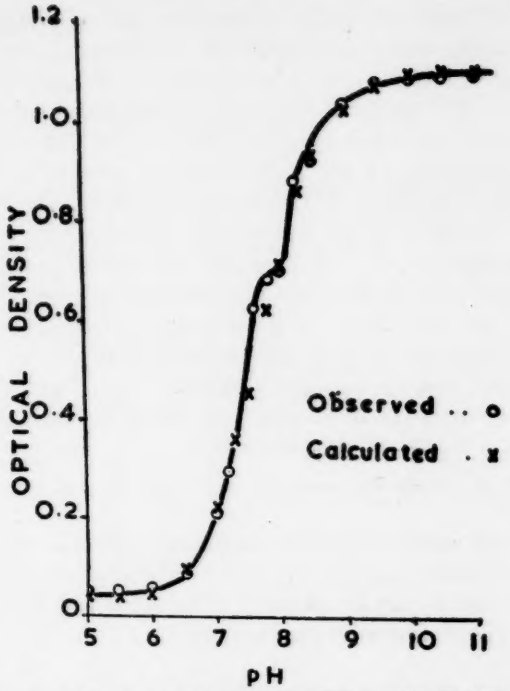


FIG. 2. Variation of optical density at $\lambda = 600$ mμ with pH of the solution.

which acts presumably as an ampholytic substance exhibiting the following equilibria:

$$^{-}HO + {}^{+}HNQOH \overset{H_2O}{\underset{(b)}{\leftrightharpoons}} NQOH \underset{(a)}{\rightleftharpoons} NQO^{-} + H^{+}$$

It can be shown that at half-transformation points of the inflexions in the curve given in Fig. 2, the pH is roughly equivalent to pK of the system; this leads to the deduction from data in Fig. 2 that pK_b and pK_a are roughly 7·3 and 8·1. It is to be noted that the system is complicated not only by the two dissociation processes but also by close proximity of the values of pK_a and pK_b, indicating that at any pH value, the optical density of the system is contributed not only by the cation or anion and neutral molecule, but by all the three forms of the substance.

The following considerations employed for calculation of the optical density at any pH value based on the values of 7·3 and 8·1 for pK_b and pK_a

referring to the basic and acidic dissociation processes respectively, are instructive: Let ϵ be the optical density of the system at any pH value. As indicated above, this is contributed by the three components of the system, *viz.*, NQOH, NQO^- and ^+HNQOH, the exact concentration of any one of these components being dependent upon the pH value of the solution. Thus in highly alkaline solutions (at $pH \geqslant 10$), it can be assumed that the entire substance (relative concentration = 1) exists in the form of anion, while in strongly acid solutions (at $pH \leqslant 5$) the cation form of the substance predominates; at any intermediate pH, it is apparent that the optical density is contributed by the appropriate portions, controlled by the dissociation constants K_a and K_b (*vide infra*) of the three forms of the substance. Let C_1, C_2 and C_0 be the concentrations of the cation, anion and uncharged components of the substance at any pH value; and E_1, E_2 and E_0 represent the relative extinction coefficients, constant characteristic quantities of the three forms, respectively, the optical density ϵ at any pH is given by

$$\epsilon = E_1C_1 + E_0C_0 + E_2C_2 \tag{1}$$

Further, from the observed optical densities at pH = 4 and 12, where the entire substance (relative concentration = 1) is in the cation and anion forms respectively, E_1 and E_2 can be assumed to be 0·035 and 1·1. The value of E_0 can be computed from the relationships that

$$pH = pK_b \log \frac{C_0}{C_1} = pK_a + \log \frac{C_2}{C_0} \tag{2}$$

and from $\epsilon = 0{\cdot}8$ at pH = 8·1 where $C_2 = C_1$; we have therefore from eq. (1) that

$$\epsilon = 0{\cdot}035\ C_1 + 0{\cdot}55\ C_0 + 1{\cdot}1\ C_2$$

The values of C_1, C_2 and C_0 for any pH value can be computed from eq. (2) and from that $C_1 + C_0 + C_2 = 1$. The values of ϵ calculated at different pH values are indicated by crosses in Fig. 2 . It was instructive to note that despite the fact that the variation of the optical density with pH was not simple, the calculated values of the optical density agreed closely with the observed data.

SUMMARY

Absorption spectra of 4-(*p*-nitrophenyl-azo)-8-hydroxy-quinoline (NQOH) in the visible region was studied at different pH values in the range 4–12. NQOH exhibited two absorption maxima, one at $\lambda = 480$ mμ in acid solution and the other at $\lambda = 600$ mμ in alkaline solution. The absorption at

$\lambda = 600$ mμ was markedly variant with the pH of the solution; the data indicated two dissociation processes presumably due to the ampholytic character of NQOH

$$^{-}HO + {}^{+}HNQOH \underset{(H_2O)}{\rightleftharpoons} NQOH \rightleftharpoons NQO^{-} + H^{+}$$

with 7·3 and 8·1 for pK_b and pK_a referring in acidic and basic dissociation processes, respectively. The optical density values calculated from these constants agreed closely with the observed data.

Acknowledgement

Authors' grateful thanks are due to Professor K. S. G. Doss, D.Sc., F.R.I.C., F.Inst.P., F.A.Sc., Director, Indian Institute of Sugar Technology, for his interest in the work.

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RAMAN SPECTRUM OF STRONTIANITE ($SrCO_3$)

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(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

The Raman spectra of crystalline carbonates have been the subject of many investigations because of the simplicity of their structure. The carbonates are of special interest as they provide data necessary for the verification of theoretical ideas concerning the influence of crystal symmetry and the cation on the vibration spectra of the CO_3 ion and the lattice. Of the orthorhombic carbonates MCO_3 (with M = Ca, Sr, Ba, Pb) strontianite which occurs as a mineral has not been studied so far. It can be expected to yield some useful information concerning the vibration spectra of orthorhombic carbonates since the polarisability of the Sr ion is intermediate between that of Ca and Pb ions (Couture, 1944 and 1947).

2. Experimental Details

Since strontianite is transparent to the ultraviolet, it was studied using the resonance radiation of mercury as exciter. A medium quartz spectrograph and a Littrow quartz spectrograph with a dispersion of about 140 and 40 wavenumbers respectively in the λ 2537 region were used in the present investigation. The specimen employed was a lump of polycrystalline strontianite and as the individual crystals were not bigger than 1 mm. in size, only a thin layer on the surface was effective in giving the scattered radiation. Exposures of the order of an hour were sufficient to get satisfactory spectra with the smaller instrument while with El (large) spectrograph 24 hours were necessary to get well exposed spectrograms.

3. Results and Discussion

The recorded Raman spectrum reveals 13 Raman lines of which 5 may be attributed to the internal oscillations of the CO_3 ions in the unit cell and the remaining 8 due to lattice oscillations. The frequency shifts are 103 (4), 115 (3), 150 (16), 184 (12), 218 (1), 238 (2), 244 (3), 254 (1), 703 (4), 1076 (20), 1406 (·5), 1438 (1) and 1449 (1), the figures within brackets indicating roughly the relative intensities. The spectrum taken with the bigger instrument is reproduced in Fig. 1 along with its microphotometer record. Even under the

high dispersion of the littrow spectrograph, the lines appear to be broad and not split up.

The structure of strontianite ($SrCO_3$) is identical with that of aragonite and belongs to the orthorhombic space group V_h^{16} (Pnma). The unit cell contains 4 molecules of $SrCO_3$. A group theoretical analysis of the vibration spectra of orthorhombic carbonates has been carried out by Bhagavantam (1941) and by Couture (1944). The main results are summarised below. Of the 57 fundamental vibrations of the unit cell 12 internal oscillations and 18 external oscillations (12 of the translational type and 6 of the rotatory type) are allowed in Raman effect.

Internal Oscillations.—The CO_3 ion in the free state has a symmetry D_{3h}. Its spectrum consists of 4 distinct frequencies ν_1, ν_2, ν_3, ν_4, the last two being doubly degenerate. The respective frequency shifts are 1080, 850, 700 and 1450 cm.$^{-1}$ Because of the lower symmetry (C_s) of the ion in strontianite the degeneracy would be removed. There may be further splitting arising from the coupling of the four ions in the unit cell. Contrary to the theoretical expectation of 12 Raman frequencies, the recorded spectrum of strontianite indicates the existence of only 5 frequencies due to internal oscillations. It can, therefore, be inferred that the splitting arising from the multiplicity of groups in the unit cell is not observed in the Raman spectrum of strontianite. Due to the irregular nature of the specimen used, the recorded spectrum was not intense enough to exhibit the octave of the inactive frequency 850 cm.$^{-1}$ Unlike in aragonite, this frequency is not observed as a fundamental in the Raman spectrum of strontianite.

Lattice Oscillations.—The observed lattice spectrum consists of 8 frequencies as compared with 14 in aragonite (Krishnan, 1950). The intense lines 150 cm.$^{-1}$ and 184 cm.$^{-1}$ may be attributed to angular oscillations of the CO_3 groups about the principal axes of inertia contained in the plane of the ion (Kastler and Rousset, 1941). It is interesting to note that, while the line arising from the oscillations about the Y-axis is nearly the same in both strontianite and aragonite (150 and 154 cm.$^{-1}$ respectively), that arising from the oscillations about the X-axis is much different (184 and 208 cm.$^{-1}$). On the basis of the principle of equipartition of energy, it is known (Couture, *loc. cit.*) that the ratio of the intensities of the two lines should be as the inverse ratio of the square of their frequency shifts. But it is experimentally found that $I_y/I_x = \cdot 75$ while $\nu_y^2/\nu_x^2 = \cdot 585$. There is, therefore, as in aragonite, only a fair agreement and the discrepancy indicates the magnitude of influence of the crystalline field.

The author's thanks are due to Prof. R. S. Krishnan for his kind interest and encouragement and to Dr. P. S. Narayanan for the valuable help given in the course of the work.

SUMMARY

The Raman spectrum of strontianite ($SrCO_3$) has been studied for the first time using the λ 2537 resonance radiation of mercury as the exciter. The observed spectrum has been compared with that of aragonite which is isomorphous with strontianite. Out of the 13 frequency shifts recorded, 5 have been attributed to the internal oscillations of the CO_3 ion and the remaining 8 to the lattice oscillations. The splitting of the degenerate ν_4 vibration of the free CO_3 ion in the crystal into 3 frequencies and also the observed relative intensity of the lines 150 cm.$^{-1}$ and 184 cm.$^{-1}$ arising from the angular oscillations of the CO_3 ions about their principal axes of inertia, indicate a considerable distortion in the symmetry of the CO_3 ion in strontianite as in the case of aragonite.

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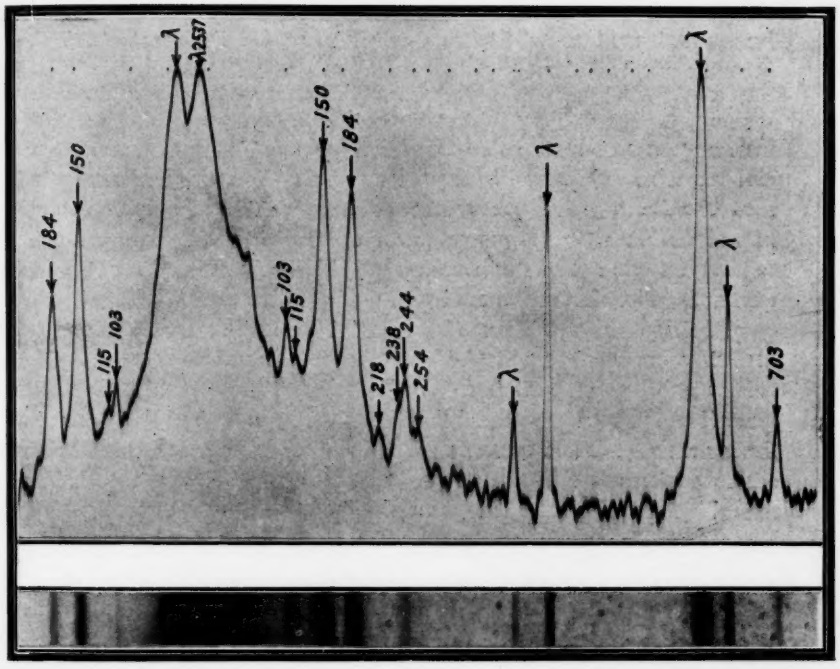

FIG. 1. (*a*) Raman spectrum of Strontianite taken with a large quartz spectrograph [E_1]; (*b*) Its microphotometer record.

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